



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 0 713 894 A3**

(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
31.07.1996 Bulletin 1996/31

(51) Int Cl.⁶: **C08G 63/91**, **C08G 63/685**,
C09D 167/04, **C09D 11/10**,
C09D 7/02

(43) Date of publication A2:
29.05.1996 Bulletin 1996/22

(21) Application number: **95402635.7**

(22) Date of filing: **22.11.1995**

(84) Designated Contracting States:
DE ES GB

(72) Inventor: **Matsui, Hideki**
Himeji-shi, Hyogo-ken (JP)

(30) Priority: **22.11.1994 JP 311302/94**
22.11.1994 JP 311303/94

(74) Representative: **Portal, Gérard et al**
Cabinet Beau de Loménie
158, rue de l'Université
75340 Paris Cédex 07 (FR)

(71) Applicant: **DAICEL CHEMICAL INDUSTRIES, LTD.**
Sakai-shi Osaka-fu 590 (JP)

(54) **A polylactone having amino groups, a process for the preparation thereof, a compound having amino group, a composition for coatings, a composition for printing inks**

(57) Disclosed are a novel polylactone having amino groups and to a process for the preparation thereof. The polylactone having amino groups of the present invention is excellent in color hue, and it can be preferably employed in fields such as coatings, inks, ultraviolet ray curable or electronic beam curable resins, etc., in which

the color hue becomes a serious problem.

Furthermore, disclosed are a novel compound having amino groups and to a process for the preparation thereof. The compound having amino groups of the present invention can be preferably employed as a dispersant for pigments in a coating composition or a printing ink composition.

EP 0 713 894 A3



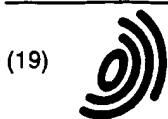
European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 40 2635

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP-A-0 115 072 (BASF AG) * claims 1-10 *	1-10	C08G63/91 C08G63/685 C09D167/04 C09D11/10 C09D7/02
A	EP-A-0 304 175 (EXXON CHEMICAL PATENTS INC)		
A	EP-A-0 624 615 (BASF AG)		
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C08G C09D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 28 May 1996	Examiner Decocker, L
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 150 (01/91) (P0101)



(19)

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 732 346 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
02.06.1999 Bulletin 1999/22

(51) Int Cl.⁶: **C08F 290/04, C09D 7/02,
C08F 220/12**

(21) Application number: **96200718.3**

(22) Date of filing: **15.03.1996**

(54) **Methacrylic copolymers and dispersants for pigments used in non-aqueous paints and varnishes comprising the copolymers**

Methacryl-Copolymere und Dispergiermittel für Pigmente, verwendet in nicht wässrigen Farben und Lacken die diese Copolymere enthalten

Copolymères methacryliques et dispersants pour pigments utilisé dans des peintures non aqueuses et vernis contenant ces copolymères

(84) Designated Contracting States:
DE FR GB NL

(30) Priority: **16.03.1995 JP 57010/95**

(43) Date of publication of application:
18.09.1996 Bulletin 1996/38

(73) Proprietor: **Kyoeisha Chemical Co., Ltd.
Osaka-shi, Osaka (JP)**

(72) Inventor: **Kawanishi, Wataru
Nara-shi, Nara (JP)**

(74) Representative:
**Smulders, Theodorus A.H.J., Ir. et al
Vereenigde Octrooibureaux
Nieuwe Parklaan 97
2587 BN 's-Gravenhage (NL)**

(56) References cited:
**EP-A- 0 269 456 EP-A- 0 491 169
GB-A- 2 029 429**

EP 0 732 346 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

[0001] The present invention relates to a methacrylic copolymer as a compound and a dispersant for pigments used in non-aqueous paints and varnishes comprising the copolymer.

[0002] The non-aqueous paints and varnishes comprise a pigment. The pigments should uniformly be dispersed within the paints and varnishes in order to ensure the formation of coated films free of any mottle. There has been known a method in which a polymer is added to paints and varnishes as a means for ensuring uniform dispersion of a pigment therein. Examples of such methods include those comprising incorporating an urethane compound carrying an amino group into paints and varnishes as disclosed in Japanese Patent Provisional Publication Nos. 62-70459, 1-135526 and 1-139132; methods comprising adding, to paints and varnishes, an isocyanate-modified acrylic polymer as disclosed in Japanese Patent Provisional Publication Nos. 63-51487 and 62-81459; and a method comprising adding, to paints and varnishes, a phosphoric acid ester derivative as disclosed in Japanese Patent Provisional Publication Nos. 63-51469.

[0003] However, the foregoing polymers are simply effective for a part of pigments and accordingly, it takes a long period of time for uniformly dispersing a pigment, in particular, carbon black having strong cohesion. When paints and varnishes comprising carbon black are stored over a long period of time, the pigment dispersed therein may sometimes cause reaggregation. For this reason, the resulting coated film may sometimes suffer from problems of mottle and reduced gloss.

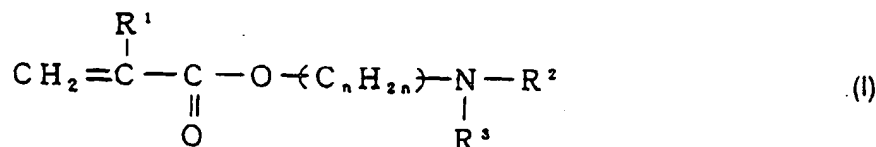
[0004] The British patent application 2 029 429 discloses pigment dispersants comprising the polymerization product of an alkyl methacrylate, a hardening monomer, an ethylenically unsaturated carboxylic acid or a monomer having a double bond α - β to a carbonyl group and which is capable of providing carboxyl functionality, a monomer having a double bond α - β to a carbonyl group and at least one hydroxyl group or a monomer capable of providing such groups and a compound providing an amine or amine salt functional moiety.

[0005] The present invention has been developed for solving the foregoing problems and accordingly, an object of the present invention is to provide a methacrylic copolymer serving as an effective component for uniformly dispersing a pigment in paints and varnishes as well as a dispersant which comprises the copolymer.

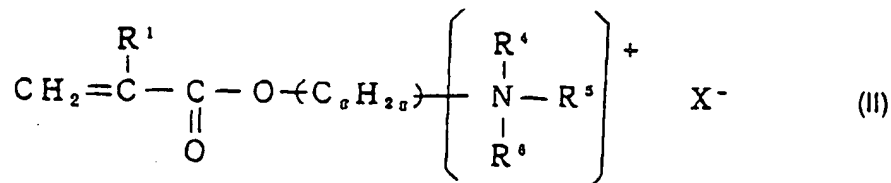
[0006] The foregoing object of the present invention can be accomplished by providing a methacrylic copolymer which is a polymer comprising repeating units derived from the following monomers:

(A) at least one (meth)acrylate monomer selected from the group consisting of alkyl (meth)acrylates each carrying an alkyl group having 1 to 18 carbon atoms; alkenyl (meth)acrylates each carrying an alkenyl group having 1 to 18 carbon atoms; hydroxyalkyl (meth)acrylates each carrying an alkyl group having 2 to 4 carbon atoms; alkyl monoalkylene glycol (meth)acrylates and alkyl polyalkylene glycol (meth)acrylates each carrying an alkyl group having 1 to 18 carbon atoms; alkenyl monoalkylene glycol (meth)acrylates and alkenyl polyalkylene glycol (meth)acrylates each carrying an alkenyl group having 1 to 18 carbon atoms; and alkylalkenyl monoalkylene glycol (meth)acrylates and alkylalkenyl polyalkylene glycol (meth)acrylates each carrying an alkylalkenyl group having 1 to 18 carbon atoms;

(B) an aminoalkyl (meth)acrylate monomer represented by the following Formula (I):



and/or a quaternary ammonium (meth)acrylate monomer represented by the following Formula (II):



(C) at least one monomer selected from the group consisting of polyalkyl (meth)acrylate macromonomers, polyalkenyl (meth)acrylate macromonomers, polyester macromonomers and polystyrene macromonomers, each carrying a terminal (meth)acryloyl group;

5 the copolymer having a content of the moieties derived from the monomer (A) ranging from 10 to 85 parts by weight, a content of the moieties derived from the monomer (B) ranging from 10 to 60 parts by weight and a content of the moieties derived from the monomer (C) ranging from 5 to 30 parts by weight and a number-average molecular weight ranging from 6000 to 50000.

[0007] In Formula (I), R^1 represents a hydrogen atom or a methyl group, R^2 and R^3 each represents a hydrogen atom or an alkyl group having 1 to 6 carbon atoms and n is an integer ranging from 2 to 8.

[0008] In Formula (II), R^4 , R^5 and R^6 which are different from one another and each represents an alkyl group having 1 to 6 carbon atoms, a hydroxyalkyl group having 2 to 6 carbon atoms, an alkoxyalkyl group having 1 to 4 carbon atoms, a cycloalkyl group, an aralkyl group, a phenyl group or a phenyl group substituted with other atoms; X^- represents a halide ion or an anionic residue of an acid; and g is an integer ranging from 2 to 8.

[0009] The European patent application 0 491 169 discloses a blister resistant pressure sensitive adhesive sheet, which comprises a coating comprising a copolymer that differs from a copolymer according to the invention in that it has a molecular weight in the range of 150,000 to 2,000,000.

[0010] Specific examples of alkyl (meth)acrylate and alkenyl (meth)acrylate monomers as the monomer component (A) include methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, hexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, isodecyl (meth)acrylate, lauryl (meth)acrylate, cyclohexyl (meth)acrylate, stearyl (meth)acrylate, benzyl (meth)acrylate and isobornyl (meth)acrylate. Specific examples of hydroxyalkyl (meth)acrylate monomers are hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate and 2-hydroxybutyl (meth)acrylate. Specific examples of alkyl monoalkylene glycol (meth)acrylate, alkyl polyalkylene glycol (meth)acrylate, alkenyl monoalkylene glycol (meth)acrylate, alkenyl polyalkylene glycol (meth)acrylate, alkylalkenyl monoalkylene glycol (meth)acrylate and alkylalkenyl polyalkylene glycol (meth)acrylate monomers are methoxy diethylene glycol (meth)acrylate, methoxy propylene glycol (meth)acrylate, n-butoxy ethylene glycol (meth)acrylate, 2-phenoxyethyl (meth)acrylate and trioxyethylene nonyl phenol (meth)acrylate.

[0011] Specific examples of aminoalkyl (meth)acrylate monomers belonging to Group (B) represented by Formula (I) are N,N-dimethylaminoethyl (meth)acrylate, N,N-diethylaminoethyl (meth)acrylate, N-tert-butylaminoethyl (meth)acrylate, N,N-dimethylaminopropyl (meth)acrylate, N,N-dimethylaminobutyl (meth)acrylate, N-propylaminoethyl (meth)acrylate and N-butylaminoethyl (meth)acrylate. The quaternary ammonium (meth)acrylate monomer represented by Formula (II) is a monomer carrying one quaternary ammonium group and one (meth)acryloyl group in the molecule. Specific examples thereof are 2-hydroxy-3-(meth)acryloxypropyl trimethylammonium chloride, 2-hydroxy-3-(meth)acryloxypropyl triethanolammonium chloride, 2-hydroxy-3-(meth)acryloxypropyl dimethylbenzylammonium chloride, 2-hydroxy-3-(meth)acryloxypropyl dimethylphenylammonium chloride, (meth)acryloxyethyl trimethylammonium chloride and (meth)acrylamidopropyl trimethylammonium chloride. In this connection, X^- is not restricted to Cl^- and therefore, the specific examples of the aminoalkyl (meth)acrylate monomers may be monomers such as those listed above comprising Br^- , I^- , F^- , HSO_4^- , SO_4^{2-} , NO_3^- , PO_4^{3-} , HPO_4^{3-} , $H_2PO_4^-$, $C_6H_5SO_3^-$ or OH^- instead of Cl^- .

[0012] Specific examples of the polyalkyl (meth)acrylate macromonomers, polyalkenyl (meth)acrylate macromonomers, polyester macromonomers and polystyrene macromonomers, each carrying a terminal (meth)acryloyl group as the monomers (C) are Macromonomer AA-6 (terminal group: methacryloyl group; segment: methyl methacrylate; number-average molecular weight: 6000; available from Toagosei Chemical Industry Co., Ltd.), Macromonomer AW-6S (terminal group: methacryloyl group; segment: isobutylmethacrylate; number-average molecular weight: 6000; available from Toagosei Chemical Industry Co., Ltd.), Macromonomer AB-6 (terminal group: methacryloyl group; segment: butyl acrylate; number-average molecular weight: 6000; available from Toagosei Chemical Industry Co., Ltd.) and Macromonomer AS-6 (terminal group: methacryloyl group; segment: styrene; number-average molecular weight: 6000; available from Toagosei Chemical Industry Co., Ltd.).

[0013] The methacrylic copolymers can be prepared by the solution polymerization. More specifically, such a methacrylic copolymer is produced by polymerizing a monomer (A), a monomer (B) and a monomer (C) in the presence of a polymerization initiator in an appropriate inert solvent. The reaction temperature preferably ranges from 70 to 150°C and more preferably 80 to 130°C and the reaction time desirably ranges from 1 to 15 hours, in particular, 4 to 8 hours.

[0014] Examples of such polymerization initiators usable herein are azo compounds such as azobisisobutyronitrile and dimethylazobisisobutyrate; and organic peroxides such as lauroyl peroxide and diisopropylbenzene hydroperoxide.

[0015] Preferably, solvents usable herein are those capable of dissolving the resulting methacrylic copolymers and likewise miscible with, for instance, paints and varnishes (hereinafter simply referred to as "paint(s)") and inks. Specific examples thereof include aromatic solvents such as xylene, Solvesso 100 and Solvesso 150; ketone type solvents such as methyl isobutyl ketone; ester type solvents such as ethyl acetate and butyl acetate; cellosolve type solvents

such as butyl cellosolve and ethyl cellosolve; propylene glycol type solvents such as propylene glycol monomethyl ether; cellosolve acetate type solvents such as ethylene glycol monoethyl ether acetate; and propylene glycol monoalkyl ether acetate type solvent such as propylene glycol monomethyl ether acetate. These solvents may be used alone or in any combination.

5 **[0016]** The dispersant for pigments used in non-aqueous paints and varnishes according to another aspect of the present invention comprises the foregoing methacrylic copolymer. More specifically, the dispersant for pigments is a solution of the foregoing methacrylic copolymer prepared by a polymerization reaction of 10 to 85 parts by weight of a monomer (A), 10 to 60 parts by weight of a monomer (B) and 5 to 30 parts by weight of a monomer (C), dissolved in a solvent such as xylene.

10 **[0017]** If the content of the monomer (A) in the methacrylic copolymer is less than 10 parts by weight, the solubility of the copolymer in a resin for paints is insufficient and the applicability of the copolymer to paints is greatly restricted. On the other hand, if it exceeds 85 parts by weight, the use of the resulting copolymer impairs the dispersion rate and the dispersion stability of pigments. If the content of the monomer (B) in the methacrylic copolymer is less than 10 parts by weight, the resulting copolymer is insufficient in the affinity for pigments and accordingly, cannot completely
15 disperse the pigments in paints, while if it exceeds 60 parts by weight, the resulting paints can simply provide coated films having low water resistance and low corrosion resistance. Finally, if the content of the monomer (C) in the methacrylic copolymer is less than 5 parts by weight, the resulting copolymer cannot completely disperse pigments in paints, while if it exceeds 30 parts by weight, the dispersion rate of pigments in paints is rather reduced.

[0018] The number-average molecular weight of the monomer (C) preferably ranges from 2000 to 20000. This is because if it is less than 2000, the copolymer has a tendency to decrease the dispersion stability of pigments. On the other hand, if it exceeds 20000, the resulting dispersant has an extremely high viscosity and cannot be practically used.

[0019] The number-average molecular weight of the methacrylic copolymer ranges from 6000 to 50000. This is because if the average molecular weight thereof is less than 6000, the physical properties of the resulting coated films may be impaired, while if it exceeds 50000, the dispersant is hard to handle because of its extremely high viscosity.

25 The molecular weight of the copolymer may easily be controlled through the use of a polymerization regulator such as an alkyl mercaptan.

[0020] The methacrylic copolymer according to the present invention is a compound effective for uniformly dispersing pigments in paints. More specifically, the copolymer can be dissolved in a solvent such as xylene, may thus serve as a dispersant for pigments used in non-aqueous paints and permits uniform dispersion of, for instance, carbon black in
30 paints. Therefore, the methacrylic copolymer and hence the dispersant of the present invention can ensure excellent coating operations and permit the formation of coated films exhibiting glossy feeling and free of any mottle, as compared with the conventional paints.

[0021] The present invention will hereinafter be described in more detail with reference to the following Examples.

35 Example 1

[0022] To an apparatus equipped with a reflux condenser, a thermometer, a stirring machine and a tank for dropwise addition, there was added 50 parts by weight of xylene and the temperature of the xylene was maintained at 100°C, followed by dropwise addition, in a nitrogen gas atmosphere, of a mixed solution comprising 30 parts by weight of ethyl
40 acrylate, 5 parts by weight of Macromonomer AA-6 (a methyl methacrylate macromonomer; available from Toagosei Chemical Industry Co., Ltd.), 15 parts by weight of Light Ester DQ-100 (a quaternary product of dimethylaminoethyl methacrylate, available from Kyoei Chemical Co., Ltd.), 0.5 part by weight of dodecyl mercaptan and 1 part by weight of azobisisobutyronitrile to the xylene over 3 hours. After completion of the addition, 0.5 part by weight of azobisisobutyronitrile was additionally added and the reaction was continued for 2 hours at 100°C to give a methacrylic copolymer.
45 The number-average molecular weight of the resulting copolymer was determined by the gel permeation chromatography and it was found to be 43000.

[0023] Then a paint base was prepared by admixing 82 part by weight of Acrydick A-801 (an acryl polyol resin; content of non-volatile matter: 50%; solvent: toluene, butyl acetate; hydroxyl value: 50; available from Dainippon Ink and Chemicals Inc.), 3.5 parts by weight of FW-200 (available from Degsa Company) as carbon black, 14.5 parts by weight of a thinner (xylene/butyl acetate = 70/30) and 1.05 part by weight of the foregoing methacrylic copolymer. The specific production processes for the base are as follows.

[0024] To a 225 ml volume glass bottle, there were added 34 g of Acrydick A-801, 4.5 g of FW-200, 19.5 g of a thinner and 1.35 g of the methacrylic copolymer as well as 200 g of glass beads having a diameter ranging from 1.5 to 2.0 mm followed by stirring them for one hour using a paint shaker (available from Red Devil Company). After one hour,
55 additional 71.6 g of Acrydick A-801 was added to the mixture, then the resulting mixture was subjected to let down, followed by removal of the glass beads through filtration to thus complete the preparation of the base.

[0025] Separately, the same procedures used above were repeated except that BP-1300 (available from Cavot Company) was substituted for the FW-200 used above to give another base. These two kinds of bases were inspected for

the viscosity, the particle size distribution, the cohesion of pigments and the gloss of the resulting coated films. The hardening agent herein used was Sumijule N-75 (available from Sumitomo Bayer Urethane Co., Ltd.).

[0026] The viscosity was determined by the following method. It was evaluated by determining shearing rates per 1.92 sec, 19.2 sec and 192 sec using a coneplate type viscometer (E Type, available from Toki Mech Co., Ltd.).

5 [0027] The particle size distribution was determined by the following method, i.e., this was evaluated through the determination of particle sizes observed when 10%, 50% and 90% of the particles passed through a measuring device, i.e., Microtruck (available from Lead & Northrup Company).

[0028] The cohesion of pigments was determined by the method which comprised introducing 10 g of a base into a 50 ml volume screw tube (having a diameter of 35 mm and a height of 78 mm), followed by sufficiently wetting the 10 inner wall of the tube, allowing the tube to stand for 24 hours and observation of the inner wall of the tube to thus determine the presence or absence of the cohesion of the pigment thereon.

[0029] The gloss of the coated film was determined by the method comprising the steps of mixing 100 parts by weight of a base and 17.6 parts by weight of Sumijule N-75, diluting the mixture with a thinner while adjusting the viscosity of the mixture to 12 sec using Ford cup #4, spray-coating the diluted paint on a tinplate sheet using an air-spraying machine, air-drying the coated layer for 24 hours and then determining the gloss at an angle of 20° of the coated plate 15 using a gloss meter to evaluate the gloss feeling of the coated film.

[0030] The evaluation results observed for the base comprising FW-200 as carbon black are likewise summarized in Table 1, while those observed for the base comprising BP-1300 as carbon black are likewise listed in Table 2.

20 Example 2

[0031] The same procedures used in Example 1 were repeated except that the mixed solution to be dropwise added to xylene comprised 30 parts by weight of 2-ethylhexyl methacrylate, 5 parts by weight of methoxy diethylene glycol methacrylate, 5 parts by weight of Macromonomer AB-6 (a butyl acrylate Macromonomer available from Toagosei 25 Chemical Industry Co., Ltd.), 10 parts by weight of Light Ester DQ-100 (a quaternary product of dimethylaminoethyl methacrylate available from Kyoei Chemical Co., Ltd.), one part by weight of dodecyl mercaptan and one part by weight of azobisisobutyronitrile to prepare a methacrylic copolymer. The number-average molecular weight of the copolymer was determined and found to be 21000.

[0032] Two kinds of bases comprising the methacrylic copolymer were likewise prepared and the resulting bases 30 were inspected for the viscosity, the particle size distribution, the cohesion of pigments and the gloss of the resulting coated films, in the same manner used in Example 1.

[0033] The evaluation results observed for the base comprising FW-200 as carbon black are likewise summarized in Table 1, while those observed for the base comprising BP-1300 as carbon black are likewise listed in Table 2.

35 Example 3

[0034] The same procedures used in Example 1 were repeated except that mixed solution to be dropwise added to xylene comprised 15 parts by weight of butyl methacrylate, 5 parts by weight of Macromonomer AA-6, 10 parts by weight of Light Ester DQ-100, 20 parts by weight of dimethylaminoethyl methacrylate, 2.5 parts by weight of dodecyl 40 mercaptan and one part by weight of azobisisobutyronitrile to prepare a methacrylic copolymer. The number-average molecular weight of the copolymer was found to be 14000.

[0035] Two kinds of bases comprising the methacrylic copolymer were prepared and the resulting bases were inspected for the viscosity, the particle size distribution, the cohesion of pigments and the gloss of the resulting coated films, in the same manner used in Example 1.

45 [0036] The evaluation results observed for the base comprising FW-200 as carbon black are likewise summarized in Table 1, while those observed for the base comprising BP-1300 as carbon black are likewise listed in Table 2.

Comparative Example 1

50 [0037] The same procedures used in Example 1 were repeated except that the mixed solution to be dropwise added to xylene comprised 25 parts by weight of butyl methacrylate, 10 parts by weight of Light Ester DQ-100, 15 parts by weight of dimethylaminoethyl methacrylate, 2.5 parts by weight of dodecyl mercaptan and one part by weight of azobisisobutyronitrile to prepare a methacrylic copolymer. The number-average molecular weight of the copolymer was determined and found to be 18000.

55 [0038] Two kinds of bases comprising the methacrylic copolymer were prepared and the resulting bases were inspected for the viscosity, the particle size distribution, the cohesion of pigments and the gloss of the resulting coated films, in the same manner used in Example 1.

[0039] The evaluation results observed for the base comprising FW-200 as carbon black are likewise summarized

in Table 1, while those observed for the base comprising BP-1300 as carbon black are likewise listed in Table 2.

Comparative Example 2

- 5 [0040] The same procedures used in Example 1 were repeated except that the mixed solution to be dropwise added to xylene comprised 46 parts by weight of lauryl methacrylate, 4 parts by weight of dimethylaminoethyl methacrylate, 0.5 parts by weight of dodecyl mercaptan and one part by weight of azobisisobutyronitrile to prepare a methacrylic copolymer. The number-average molecular weight of the copolymer was determined and found to be 32000.
- 10 [0041] Two kinds of bases comprising the methacrylic copolymer were prepared and the resulting bases were inspected for the viscosity, the particle size distribution, the cohesion of pigments and the gloss of the resulting coated films, in the same manner used in Example 1.
- [0042] The evaluation results observed for the base comprising FW-200 as carbon black are summarized in Table 1, while those observed for the base comprising BP-1300 as carbon black are listed in Table 2.

15 Comparative Example 3

- [0043] The same procedures used in Example 1 were repeated except that the mixed solution to be dropwise added to xylene comprised 10 parts by weight of butyl methacrylate, 40 parts by weight of dimethylaminoethyl methacrylate, 0.5 parts by weight of dodecyl mercaptan and one part by weight of azobisisobutyronitrile to prepare a methacrylic copolymer. The number-average molecular weight of the copolymer was determined and found to be 24000.
- 20 [0044] Two kinds of bases comprising the methacrylic copolymer were prepared and the resulting bases were inspected for the viscosity, the particle size distribution, the cohesion of pigments and the gloss of the resulting coated films, in the same manner used in Example 1.
- [0045] The evaluation results observed for the base comprising FW-200 as carbon black are summarized in Table 1, while those observed for the base comprising BP-1300 as carbon black are listed in Table 2.

Comparative Example 4

- 30 [0046] Two kinds of bases were prepared by the same method used in Example 1 except that Disperbyk 160 (a cationic polyurethane polymer available from Big Chemie Company) was substituted for the methacrylic copolymer and the resulting bases were inspected for the viscosity, the particle size distribution, the cohesion of pigments and the gloss of the resulting coated films, in the same manner used in Example 1. The evaluation results observed for the base comprising FW-200 as carbon black are summarized in Table 1, while those observed for the base comprising BP-1300 as carbon black are listed in Table 2.

Comparative Example 5

- 40 [0047] Two kinds of bases were prepared by the same method used in Example 1 except that Anti-tera U (a salt of a long chain polyaminoamide with a high molecular weight acid ester, available from Big Chemie Company) was substituted for the methacrylic copolymer and the resulting bases were inspected for the viscosity, the particle size distribution, the cohesion of pigments and the gloss of the resulting coated films, in the same manner used in Example 1. The evaluation results observed for the base comprising FW-200 as carbon black are summarized in Table 1, while those observed for the base comprising BP-1300 as carbon black are listed in Table 2.

45 Blank Test

- [0048] A base as a blank was prepared by the same method used in Example 1 except that any methacrylic copolymer was not used at all and the resulting blank was inspected for viscosity, particle size distribution, cohesion of pigments and gloss of the resulting coated films, in the same manner used in Example 1. The evaluated results on the base comprising FW-200 as carbon black are likewise summarized in Table 1, while those observed for the base comprising BP-1300 as carbon black are likewise listed in Table 2.

55

Table 1

Ex. No.	Viscosity of Base(mPa.s)			Particle Size Distribution(μm)			Cohesion of Pigment	Result 20° Gloss Determination
	1.92 s ⁻¹	19.2 s ⁻¹	192 s ⁻¹	10% Pass	50% Pass	90% Pass		
1	250	152	98.5	0.20	0.35	0.50	not observed	92.2
2	150	92.5	85.0	0.15	0.25	0.33	not observed	92.5
3	180	135	92.3	0.18	0.32	0.45	not observed	92.0
1*	850	320	200	0.20	0.50	1.05	observed	88.5
2*	1500	640	420	0.32	0.93	2.25	observed	85.2
3*	820	505	310	0.22	0.48	0.95	observed	87.0
4*	1950	696	512	0.39	0.90	3.04	observed	83.2
5*	6140	1450	649	0.68	2.25	5.38	observed	80.1
Blank	3280	860	541	0.28	0.98	2.36	observed	87.7

*: Comparative Example

Table 2

Ex. No.	Viscosity of Base(mPa.s)			Particle Size Distribution(μm)			Cohesion of Pigment	Result of 20° Gloss Determination
	1.92 s ⁻¹	19.2 s ⁻¹	192 s ⁻¹	10% Pass	50% Pass	90% Pass		
1	540	370	355	0.25	0.48	0.75	not observed	88.0
2	495	343	330	0.22	0.40	0.63	not observed	88.5
3	520	360	350	0.24	0.45	0.72	not observed	88.2
1*	850	615	365	0.42	0.95	1.83	observed	84.8
2*	1050	640	410	0.78	1.65	3.85	observed	81.2
3*	960	625	400	0.38	0.90	1.78	observed	82.8
4*	1740	659	453	0.52	1.35	3.10	observed	80.4
5*	3480	969	520	1.36	2.52	6.03	observed	83.1
Blank	1020	553	366	0.58	1.94	6.87	observed	85.1

*: Comparative Example

[0049] As seen from the results listed in Tables 1 and 2, the paints of Examples 1 to 3 each exhibited a low viscosity and a narrow particle size distribution as compared with those observed for the paints of Comparative Examples 1 to 5 and Blanks. Moreover, the former did not cause any cohesion of the pigment on the inner wall of the bottle and the resulting coated films were improved in the gloss. Accordingly, it is confirmed that the methacrylic copolymers prepared in Examples 1 to 3 are effective for use as dispersants for pigments.

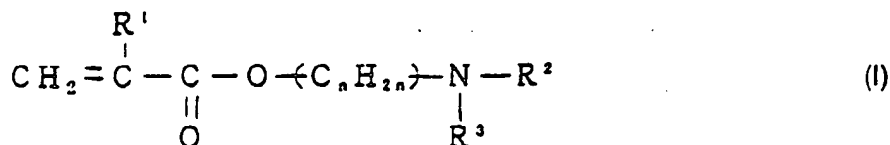
Claims

1. A methacrylic copolymer comprising repeating units derived from the following monomers:

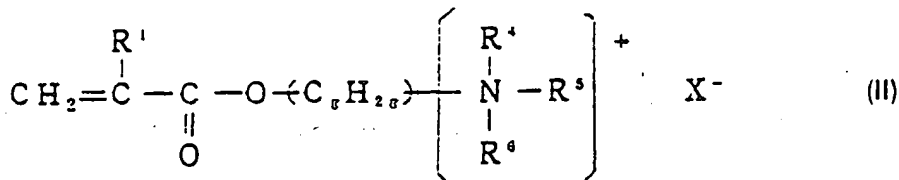
A) at least one (meth)acrylate monomer selected from the group consisting of alkyl (meth)acrylates each carrying an alkyl group having 1 to 18 carbon atoms; alkenyl (meth)acrylates each carrying an alkenyl group

having 1 to 18 carbon atoms: hydroxyalkyl (meth)acrylates each carrying an alkyl group having 2 to 4 carbon atoms; alkyl monoalkylene glycol (meth)acrylates and alkyl polyalkylene glycol (meth)acrylates each carrying an alkyl group having 1 to 18 carbon atoms; alkenyl monoalkylene glycol (meth)acrylates and alkenyl polyalkylene glycol (meth)acrylates each carrying an alkenyl group having 1 to 18 carbon atoms; and alkylalkenyl monoalkylene glycol (meth)acrylates and alkylalkenyl polyalkylene glycol (meth)acrylates each carrying an alkylalkenyl group having 1 to 18 carbon atoms;

(B) an aminoalkyl (meth)acrylate monomer represented by the following Formula (I):



(wherein R¹ represents a hydrogen atom or a methyl group, R² and R³ each represents a hydrogen atom or an alkyl group having 1 to 6 carbon atoms and n is an integer ranging from 2 to 8), and/or a quaternary ammonium (meth)acrylate monomer represented by the following Formula (II):



wherein R⁴, R⁵ and R⁶ which are different from one another and each represents an alkyl group having 1 to 6 carbon atoms, a hydroxyalkyl group having 2 to 6 carbon atoms, an alkoxyalkyl group having 1 to 4 carbon atoms, a cycloalkyl group, an aralkyl group, a phenyl group or a phenyl group substituted with other atoms; X⁻ represents a halide ion or an anionic residue of an acid; and g is an integer ranging from 2 to 8) and (C) at least one monomer selected from the group consisting of polyalkyl (meth)acrylate macromonomers, polyalkenyl (meth)acrylate macromonomers, polyester macromonomers and polystyrene macromonomers, each carrying a terminal (meth)acryloyl group; the copolymer having a content of the moieties derived from the monomer (A) ranging from 10 to 85 parts by weight, a content of the moieties derived from the monomer (B) ranging from 10 to 60 parts by weight and a content of the moieties derived from the monomer (C) ranging from 5 to 30 parts by weight and a number-average molecular weight ranging from 6000 to 50000.

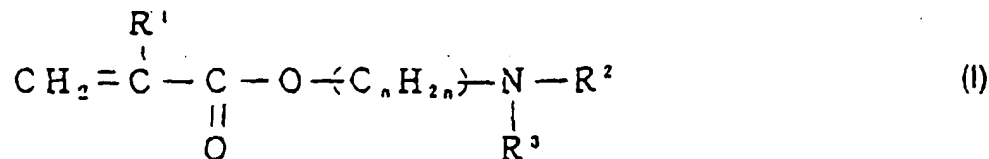
2. A dispersant for dispersing pigments in non-aqueous paints and varnishes comprising a methacrylic copolymer according to claim 1.

Patentansprüche

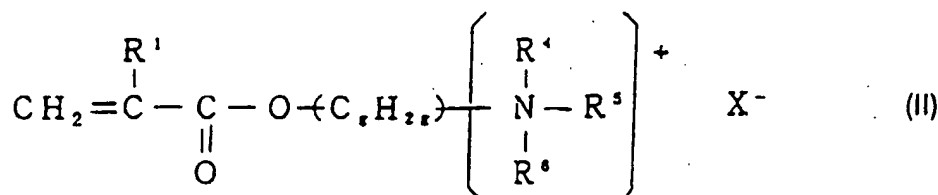
1. Methacryl-Copolymer, umfassend Grundeinheiten, die von den folgenden Monomeren abgeleitet sind:

(A) mindestens ein (Meth)Acrylat-Monomer, ausgewählt aus der Gruppe, bestehend aus Alkyl(meth)acrylaten, von denen jedes eine Alkylgruppe mit 1 bis 18 Kohlenstoffatomen trägt; Alkenyl(meth)acrylaten, von denen jedes eine Alkenylgruppe mit 1 bis 18 Kohlenstoffatomen trägt; Hydroxyalkyl(meth)acrylaten, von denen jedes eine Alkylgruppe mit 2 bis 4 Kohlenstoffatomen trägt; Alkylmonoalkylenglykol(meth)acrylaten und Alkylpolyalkylenglykol(meth)acrylaten, von denen jedes eine Alkylgruppe mit 1 bis 18 Kohlenstoffatomen trägt; Alkenylmonoalkylenglykol(meth)acrylaten und Alkenylpolyalkylenglykol(meth)acrylaten, von denen jedes eine Alkenylgruppe mit 1 bis 18 Kohlenstoffatomen trägt; und Alkylalkenylmonoalkylenglykol(meth)acrylaten und Alkylalkenylpolyalkylenglykol(meth)acrylaten, von denen jedes eine Alkylalkenylgruppe mit 1 bis 18 Kohlenstoffatomen trägt;

(B) ein Aminoalkyl(meth)acrylat-Monomer, dargestellt durch die folgende Formel (I):



(in der R¹ ein Wasserstoffatom oder eine Methylgruppe darstellt, jede der Gruppen R² und R³ ein Wasserstoffatom oder eine Alkylgruppe mit 1 bis 6 Kohlenstoffatomen darstellt und n eine ganze Zahl ist, die von 2 bis 8 reicht), und/oder ein quartäres Ammonium(meth)acrylat-Monomer, dargestellt durch die folgende Formel(II):



(in der jede der Gruppen R⁴, R⁵ und R⁶, die verschieden voneinander sind, eine Alkylgruppe mit 1 bis 6 Kohlenstoffatomen, eine Hydroxyalkylgruppe mit 2 bis 6 Kohlenstoffatomen, eine Alkoxyalkylgruppe mit 1 bis 4 Kohlenstoffatomen, eine Cycloalkylgruppe, eine Arylgruppe, eine Phenylgruppe oder eine mit anderen Atomen substituierte Phenylgruppe darstellen; X ein Halogenid-Ion oder einen anionischen Rest einer Säure darstellt; und g eine ganze Zahl ist, die von 2 bis 8 reicht) und

(C) mindestens ein Monomer, ausgewählt aus der Gruppe, bestehend aus Polyalkyl(meth)acrylat-Makromonomeren, Polyalkenyl(meth)acrylat-Makromonomeren, Polyester-Makromonomeren und Polystyrol-Makromonomeren, von denen jedes eine terminale (Meth)acryloylgruppe trägt; wobei das Copolymer einen Gehalt an von dem Monomer (A) abgeleiteten Gruppen hat, der von 10 bis 85 Gewichtsteile reicht, einen Gehalt an von dem Monomer (B) abgeleiteten Gruppen hat, der von 10 bis 60 Gewichtsteile reicht, und einen Gehalt an von dem Monomer (C) abgeleiteten Gruppen hat, der von 5 bis 30 Gewichtsteile reicht, und ein Zahlenmittel des Molekulargewichts hat, das von 6000 bis 50000 reicht.

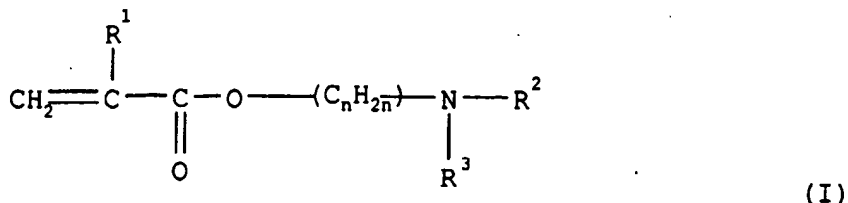
2. Dispergiermittel zur Dispersion von Pigmenten in nichtwässrigen Farben und Lacken, umfassend ein Methacryl-Copolymer nach Anspruch 1.

Revendications

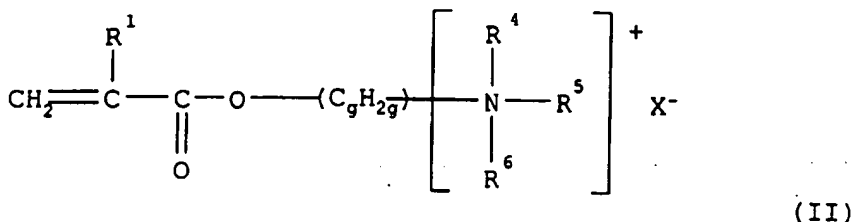
1. Copolymère méthacrylique comprenant des motifs répétitifs dérivés des monomères suivants :

(A) au moins un monomère (méth)acrylate choisi parmi le groupe constitué des (méth)acrylates d'alkyle portant chacun un groupe alkyle ayant 1 à 18 atomes de carbone ; des (méth)acrylates d'alcényle portant chacun un groupe alcényle ayant 1 à 18 atomes de carbone ; des (méth)acrylates d'hydroxyalkyle portant chacun un groupe alkyle ayant 2 à 4 atomes de carbone ; des (méth)acrylates d'alkyl-monoalkylène glycol et des (méth)acrylates d'alkylpolyalkylène glycol portant chacun un groupe alkyle ayant 1 à 18 atomes de carbone ; des (méth)acrylates d'alcénylmonoalkylène glycol et des (méth)acrylates d'alcénylpolyalkylène glycol portant chacun un groupe alcényle ayant 1 à 18 atomes de carbone ; et des (méth)acrylates d'alkylalcényl-monoalkylène glycol et des (méth)acrylates d'alkylalcényl-polyalkylène glycol portant chacun un groupe alkylalcényle ayant 1 à 18 atomes de carbone ;

(B) un monomère (méth)acrylate d'aminoalkyle représenté par la Formule (I) suivante :



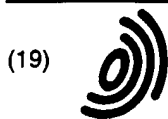
(dans laquelle R^1 représente un atome d'hydrogène ou un groupe méthyle, R^2 et R^3 représentent chacun indépendamment un atome d'hydrogène ou un groupe alkyle ayant 1 à 6 atomes de carbone et n est un entier compris entre 2 et 8), et/ou un monomère (méth)acrylate d'ammonium quaternaire représenté par la Formule (II) suivante :



(dans laquelle R^4 , R^5 et R^6 sont différents les uns des autres et représentent chacun indépendamment un groupe alkyle ayant 1 à 6 atomes de carbone, un groupe hydroxyalkyle ayant 2 à 6 atomes de carbone, un groupe alkoxyalkyle ayant 1 à 4 atomes de carbone, un groupe cycloalkyle, un groupe aralkyle, un groupe phényle ou un groupe phényle substitué par d'autres atomes; X représente un ion halogénure ou un fragment anionique d'un acide; et g est un entier compris entre 2 et 8) et

(C) au moins un monomère choisi parmi le groupe constitué des macromonomères (méth)acrylates de polyalkyle, des macromonomères (méth)acrylates de polyalcényle, des macromonomères polyester et des macromonomères polystyrènes, chacun portant un groupe (méth)acryloyle terminal; le copolymère ayant une teneur en fragments dérivés du monomère (A) comprise entre 10 et 85 parties en poids, une teneur en fragments dérivés du monomère (B) comprise entre 10 et 60 parties en poids et une teneur en fragments dérivés du monomère (C) comprise entre 5 et 30 parties en poids et un poids moléculaire moyen en nombre compris entre 6000 et 50 000.

2. Dispersant pour disperser des pigments dans des peintures et vernis non aqueux comprenant un copolymère méthacrylique selon la revendication 1.



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 0 713 894 A2**

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
29.05.1996 Bulletin 1996/22

(51) Int Cl.⁶: **C08G 63/91, C08G 63/685,
C09D 167/04, C09D 11/10**

(21) Application number: **95402635.7**

(22) Date of filing: **22.11.1995**

(84) Designated Contracting States:
DE ES GB

(72) Inventor: **Matsui, Hideki**
Himeji-shi, Hyogo-ken (JP)

(30) Priority: **22.11.1994 JP 311302/94**
22.11.1994 JP 311303/94

(74) Representative: **Portal, Gérard et al**
Cabinet Beau de Loménie
158, rue de l'Université
75340 Paris Cédex 07 (FR)

(71) Applicant: **DAICEL CHEMICAL INDUSTRIES, LTD.**
Sakai-shi Osaka-fu 590 (JP)

(54) **A polylactone having amino groups, a process for the preparation thereof, a compound having amino group, a composition for coatings, a composition for printing inks**

(57) Disclosed are a novel polylactone having amino groups and to a process for the preparation thereof. The polylactone having amino groups of the present invention is excellent in color hue, and it can be preferably employed in fields such as coatings, inks, ultraviolet ray curable or electronic beam curable resins, etc., in which the color hue becomes a serious problem.

Furthermore, disclosed are a novel compound having amino groups and to a process for the preparation thereof. The compound having amino groups of the present invention can be preferably employed as a dispersant for pigments in a coating composition or a printing ink composition.

EP 0 713 894 A2

Description**FIELD OF THE INVENTION**

5 The present invention relates to a polylactone having amino groups and to a process for the preparation thereof.
The polylactone having amino groups of the present invention can be employed as an emulsified urethane and a dispersant for pigments, etc.

Furthermore, the present invention relates to a process for the preparation of the polylactone having amino groups.

10 Still further, the present invention relates to a compound having amino groups prepared by the reaction of a polyester compound in which there is included a structural unit having a functional group capable of reacting with amino groups by a Michael addition reaction at terminal, with a polyamine compound.

In addition, the present invention relates to a dispersant for pigments, a composition for coatings, and a composition for printing inks which essentially contain the compound having amino groups.

BACKGROUND OF THE INVENTION

A large amount of polyurethane resins have been used in a variety of fields such as resins for coatings, adhesives, dispersants for inks, ultraviolet ray curable or electronic beam curable resins, and foams, etc.

20 Among the urethane resins, those urethane resins having lactone chains in the main structure have been widely employed because of their excellent properties.

In the case when the urethane resin having lactone chains is modified as a hydrophilic urethane resin for the purpose of preparing water-based inks or coatings, it has been carried out that amino groups are introduced into the urethane resin.

25 Also, in the case of intending to improve an anti-strippability of coatings or adhesives from a substrate, and in the case of intending to improve dispersity of inorganic fillers such as magnetic powders in a urethane resin as a binder for magnetic tapes, there has been carried out the introduction of amino groups into the urethane resin.

For example, Japanese Patent Kokai No. 62-218456 discloses that a polycaprolactone having amino groups and urethane resins therefrom can be prepared by the addition reaction of lactone monomers to diamines such as methylinobisethylene diamine, etc. or to an aminoalcohol such as N-methyldiethanol amine.

30 It has been conventionally known that lactone monomers can be introduced into hydroxyl group and amino groups by ring-opening addition polymerization, and lactones having amino groups have been prepared by the addition polymerization of lactone monomers to amino alcohol, etc., by heating at 100 to 200°C in the presence of catalysts.

However, in the case when amines are allowed to thermally react at the above-mentioned reaction conditions, the polycaprolactone having amino groups which is a resulting polymer in a succeeding step is colored, inevitably resulting in that a urethane resin prepared therefrom is also colored.

35 Although the coloration can be prevented by preparing the polycaprolactone by the reaction at a temperature below 100°C, reaction period is considerably lengthened, unpreferably resulting in becoming problematic from a viewpoint of commercial production.

40 The coloration is a serious problem in the case when the polyurethane resin is employed as resins for coatings, inks, ultraviolet ray curable or electronic beam curable resins, etc., and even though excellent properties are obtained in the urethane resins, the colored polylactone having amino groups cannot be substantially employed.

Furthermore, as the polylactone having amino groups derived from a diamine has amide groups, a cohesive force becomes strong. As the result, in the case when lactone chains are short, it unpreferably results in becoming poor in solubility in solvents and compatibility with other resins.

45 In the meantime, a variety of dispersants have been employed for the purpose of improving dispersity of pigments and storage stability of coatings, reducing a period for dispersing, preventing separation of pigments or dyes, and improving gloss of coated layer or printed surface in the use of coating compositions and inks. Generally speaking, the dispersants to be employed for such purposes contain functional groups capable of adsorbing pigments and polymer chains composed of polyester or acrylic units having a good compatibility with vehicles for coatings or inks.

50 There are disclosed a variety of dispersants having amino groups as the functional groups capable of adsorbing pigments.

For example, Japanese Patent Kokai No. 103988/1978 discloses amino compounds having a low molecular weight such as N,N-dimethylaminopropylamine, and Japanese Patent Kokai No. 174939/1986 discloses dispersants for pigments comprising a polyethylene imine which is an amine compound having a high molecular weight. These dispersants 55 for pigments have molecular structures in which polyester chains are combined with polyamines through amide bonds. However, compounds having amide bonds are very strong in cohesive force, as the result, there are problems that the compounds are low in solubility into many solvents for coatings.

Furthermore, nitrogens in the amide bonds do not exhibit adsorption onto pigments because nitrogens in the amide

bonds are exceedingly weak in basicity.

For the purpose of improving stability in dispersity by effectively forming a sterically repulsive layer on the surface of pigments, there can be possibly thought an attempt that many amounts of polyester chains are grafted to polyamine chains.

5 However, grafting of polyester chains results in decreasing the amount of functional groups for adsorbing, resulting in causing a problem of decreasing dispersity.

Furthermore, a reaction for grafting polyester chains to polyamine chains requires a temperature ranging from 100 to 150°C at the lowest in order to attain an appropriate reaction rate.

10 When starting materials containing amines are heated at the reaction temperature, coloring of a reaction product is almost unavoidable. Accordingly, in light colored coatings, particularly in white colored coatings, it results in becoming problematic.

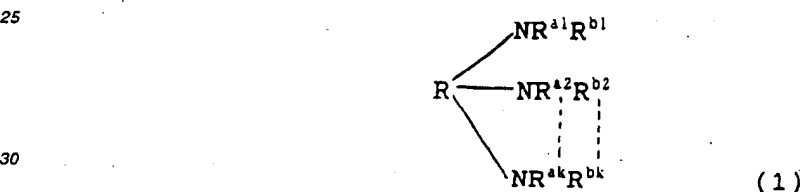
In view of such situations, and as a result of extensive investigations, the present inventor has now completed the present invention.

15 SUMMARY OF THE INVENTION

It is an object of the present invention to provide a polylactone having amino groups which is colorless and excellent in compatibility with other polymers and solubility in solvents, and which can be conveniently employed in a field in which colorless products are required, and it is another object to a process for the preparation thereof.

20 It is a third object of the present invention to provide a compound having amino groups which can be preferably employed as dispersants for coatings or printing inks.

A first aspect of the present invention relates to a polylactone having amino groups represented by the general formula (1)

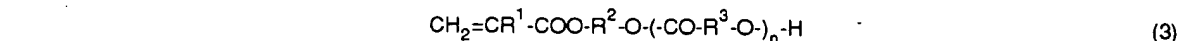


wherein R is a residual group of an aliphatic, alicyclic, or aromatic hydrocarbon, the atom N may form a ring together with said R which may have a substituent group, at least one of R^{a1}, R^{a2}, ..., R^{ak}, R^{b1}, R^{b2}, ..., R^{bk} is a substituent group represented by the general formula (2)



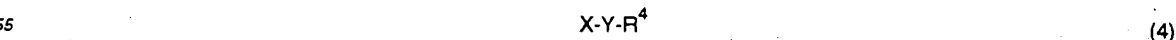
wherein R¹ is a hydrogen or methyl group, R² is a residual group of an aliphatic or aromatic hydrocarbon having a carbon number ranging from 1 to 10, polypropyleneoxy units or polyethyleneoxy units which may have substituent groups, R³ is an alkylene unit having a carbon number ranging from 3 to 10 which may have side chains having a carbon number ranging from 1 to 5, n pieces of R³ may be identical or different from each other, n is a number ranging from 1 to 100 on an average, and other R^{a1}, R^{a2}, ..., R^{ak}, R^{b1}, R^{b2}, ..., R^{bk} are independently a hydrogen or an alkyl group having a carbon number ranging from 1 to 10, k is an integer ranging from 1 to 5.

40 A second aspect of the present invention relates to a process for the preparation of the polylactone having amino groups which comprises a Michael addition reaction of a polylactone having (meth)acrylic group represented by the general formula (3)



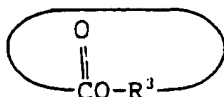
wherein R¹ is a hydrogen or methyl group, R² is a residual group of an aliphatic, alicyclic, or aromatic hydrocarbon having a carbon number of 1 to 10, polypropyleneoxy units or polyethyleneoxy units which may have substituent groups, R³ is an alkylene unit which may have side chains having a carbon number of 1 to 5, n pieces of R³ may be identical or different from each other, n is a number of 1 to 100 on an average, with an amine having a primary amino group or secondary amino group.

A third aspect of the present invention relates to a compound having amino groups prepared by the reaction of a polyester compound represented by the general formula (4)



wherein X is a structural unit having a functional group capable of reacting with amino groups by a Michael addition reaction at terminal, R⁴ is an alkyl group having a carbon number ranging from 1 to 20, an aromatic group, hydroxyl group, cyano group, and halogen atom, and Y is a structural unit having a polyester chain derived from a lactone

compound represented by the general formula (5)



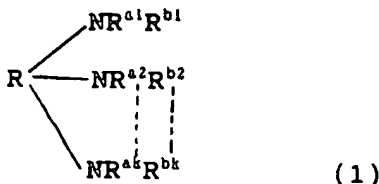
wherein R^3 is an alkylene group having a carbon number ranging from 1 to 10 which may be substituted by an aliphatic alkyl group having a carbon number ranging from 1 to 20, with a polyamine compound.

A fourth aspect of the present invention relates to a dispersant for pigments containing the compound having amino groups. A fifth aspect of the present invention relates to a composition for coatings containing the compound having amino groups. A sixth aspect of the present invention relates to a composition for inks containing the compound having amino groups.

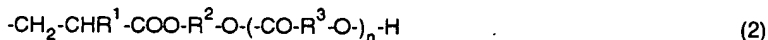
DETAILED DESCRIPTION OF THE INVENTION

The present invention will be described hereinafter in more detail.

According to a first aspect of the present invention, there is provided a polylactone having amino groups represented by the general formula (1)

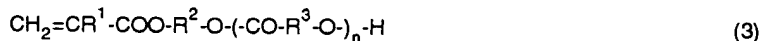


wherein R is a residual group of an aliphatic, alicyclic, or aromatic hydrocarbon, the atom N may form a ring together with said R which may have a substituent group, at least one of R^{a1} , R^{a2} , ..., R^{ak} , R^{b1} , R^{b2} , ..., R^{bk} are a substituent group represented by the general formula (2)



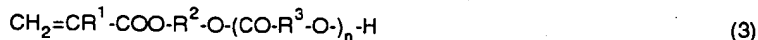
wherein R^1 is a hydrogen or methyl group, R^2 is a residual group of an aliphatic or aromatic hydrocarbon having a carbon number ranging from 1 to 10, polypropyleneoxy units or polyethyleneoxy units which may have substituent groups, R^3 is an alkylene unit having a carbon number ranging from 3 to 10 which may have side chains having a carbon number ranging from 1 to 5, n pieces of R^3 may be identical or different from each other, n is a number ranging from 1 to 100 on an average, and other R^{a1} , R^{a2} , ..., R^{ak} , R^{b1} , R^{b2} , ..., R^{bk} are independently a hydrogen or an alkyl group having a carbon number ranging from 1 to 10, k is an integer ranging from 1 to 5.

According to a second aspect of the present invention, there is provided a process for the preparation of the polylactone having amino groups which comprises a Michael's addition reaction of a polylactone having (meth)acrylic group represented by the general formula (3)



wherein R^1 is a hydrogen or methyl group, R^2 is a residual group of an aliphatic, alicyclic, or aromatic hydrocarbon having a carbon number of 1 to 10, polypropyleneoxy units or polyethyleneoxy units which may have substituent groups, R^3 is an alkylene unit which may have side chains having a carbon number of 1 to 5, n pieces of R^3 may be identical or different from each other, n is a number of 1 to 100 on an average, with an amine having a primary amino group or secondary amino group.

The polylactone having (meth)acrylic group represented by the general formula (3)



which is one starting material can be prepared by addition reaction of lactone compounds to a (meth)acrylate having hydroxyl group.

As the (meth)acrylate having hydroxyl group, there can be employed hydroxyethyl(meth)acrylate, hydroxypropyl(meth)acrylate, hydroxybutyl(meth)acrylate, polyethyleneglycol mono(meth)acrylate, polypropyleneglycol mono(meth)acrylate, polyethyleneglycol-propyleneglycol mono(meth)acrylate, polyethyleneglycol-polytetramethyleneglycol mono(meth)acrylate, polypropyleneglycol-polytetramethyleneglycol mono(meth)acrylate (eg. Blemmer PE, Blemmer PP family manufactured by Nihon Yushi, Co. Ltd.)

As the lactone compounds, there can be employed epsilon-caprolactone, delta-valerolactone, beta-methyl-delta-Valerolactone, 4-methylcaprolactone, 2-methylcaprolactone, beta-propiolactone, gamma-butyrolactone.

One or more of the lactone compounds may be employed.

In the case when a lactone (meth)acrylate having a high molecular weight is prepared by using only the lactone compound not having side chains, there is obtained a lactone (meth)acrylate which is solid at ordinary temperatures. On the other hand, in the case when a lactone (meth)acrylate having high molecular weight is prepared by using lactone compounds mixed with the lactone compound having side chains, there can be obtained a lactone (meth)acrylate which is liquid-state at ordinary temperatures.

The addition reaction of the lactone compounds can be carried out by charging the (meth)acrylate having hydroxyl group and lactone compounds into a reaction vessel equipped with a condenser, an agitator, a thermometer, and a tube for supplying air or oxygen.

The reaction temperature ranges from 50 to 150°C, preferably from 80 to 120°C. In the case when it is below 50°C, the reaction rate is slow and, contrarily, in the case when it exceeds 150°C, the (meth)acrylate having hydroxyl group polymerizes, resulting in being incapable of obtaining a desired product.

The reaction is carried out in the presence of catalysts.

As the catalysts to be employed, there are exemplified a titanium-based catalyst such as tetrabutyl titanate and tetraisopropyl titanate, a tin-based catalyst such as stannous chloride, stannous octylate, and monobutyl tin oxide, an acid-based catalyst such as p-toluenesulfonic acid, etc.

The catalysts are employed in an amount ranging from 0.1 to 3000 ppm, preferably from 1 to 100 ppm. In the case when the amount is below 0.1 ppm, the reaction rate is too slow and, contrarily, in the case when it exceeds 3000 ppm, the resulting product is colored and becomes unstable.

The reaction is carried out in the presence of polymerization inhibitors in order to prevent polymerization of the (meth)acrylates having hydroxyl group.

As the polymerization inhibitors to be employed, there are exemplified hydroquinone, methylhydroquinone, and phenothiazine, etc. which are conventional polymerization inhibitors.

Furthermore, the reaction is also employed in the presence of a small amount of oxygen as polymerization inhibitors in order to prevent polymerization of the (meth)acrylates having hydroxyl group.

For example, in the case when 1 mol of hydroxyethyl methacrylate and 2 mol of epsilon-caprolactone are employed as starting materials, there is obtained the polylactone having methacrylic group represented by the formula $\text{CH}_2=\text{C}(\text{CH}_3)\text{-COO-CH}_2\text{CH}_2\text{-O-[-CO-(CH}_2)_5\text{-O]}_2\text{-H}$ which is known as PCL-FM2 manufactured by Daicel Chemical Industries, Ltd.

Thus-obtained the polylactone having the (meth)acrylic group is allowed to react with amines to obtain the lactone compound having amino groups represented by the above-described general formula (1) of the present invention.

The amines to be employed essentially includes primary or secondary amino groups, and amines having two functionalities are preferably employed in order to prepare a starting material for polyurethanes.

Examples of amines are: ethylenediamine, N,N'-dimethylethylenediamine, piperazine, piperazine derivatives such as 2-methylpiperazine, 2,5-dimethylpiperazine, 2,3-dimethylpiperazine, 1,4-bis(3-aminopropyl)piperazine, N-aminoethylpiperazine, isophoronediamine, polyoxypropylenediamine, bis(4-amino-3-methyldicyclohexyl)methane, diaminodicyclohexylmethane, bis(aminomethyl)cyclohexane, m-xylylenediamine, alpha-(m-aminophenyl)ethylamine, alpha-(p-aminophenyl)ethylamine, metaphenylenediamine, diaminodiphenylmethane, diaminodiphenylsulfone, norbornenediamine, etc., which include conventional aliphatic, alicyclic, and aromatic amines.

Amination reaction is carried out by charging the above-mentioned amines and the lactone-modified (meth)acrylates having hydroxyl group at the same time into a reaction vessel equipped with a tube for removing water, a condenser, and a dropwise funnel, or by charging either the amine or the (meth)acrylate into the reaction vessel and charging the either into the dropwise funnel for adding dropwise.

Amination reaction slightly exothermally, nearly quantitatively, and quickly proceeds even at room temperatures.

As the amination reaction quantitatively proceeds, the amine and the lactone-modified (meth)acrylate having hydroxyl group can be employed in the molar ratio of nearly 1/1. The reaction temperature generally ranges from 10 to 130°C, preferably from 20 to 100°C.

In the case when the temperature is below 10°C, the reaction rate is slow, resulting in becoming industrially disadvantageous and, contrarily, in the case when it exceeds 130°C, functional groups capable of reacting by a Michael addition react with each other, resulting in causing a problem of coloring in a product.

In the amination reaction, inert solvents can be employed. As examples of the solvents, there can be exemplified aromatic solvents such as xylene, toluene, Solvesso, ketones such as acetone, methylethylketone, methylisobutylketone, alcohols such as butanol and isopropanol, esters such as dimethyladipate, dimethylsuccinate, and dimethylglutarate.

Although the solvents employed in the reaction may be removed by evaporation after the completion of the reaction, the solvents may be employed as components in products.

Thus-obtained polylactone having amino groups of the present invention represented by the above-described the general formula (1) is excellent in color hue, and it can be preferably employed in the fields such as coatings, inks, ultraviolet ray curable or electronic beam curable resins, etc., in which the color hue becomes a serious problem.

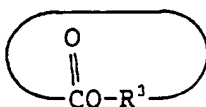
For example, polyurethanes prepared from the polylactone having amino groups of the present invention have a more excellent anti-strippability from a substrate and a more excellent dispersibility for pigments than polyurethanes having amino groups prepared from amino alcohols having short chains.

Furthermore, according to the preparation process of the present invention, the polylactone having amino groups which is low in color hue can be prepared by an exceedingly mild condition and short reaction time of period, resulting in being industrially advantageous.

According to a third aspect of the present invention, there is provided a compound having amino groups prepared by the reaction of a polyester compound represented by the general formula (4)



wherein X is a structural unit having a functional group capable of reacting with amino groups by a Michaels addition reaction at terminal, R^4 is an alkyl group having a carbon number ranging from 1 to 20, an aromatic group, hydroxyl group, cyano group, and halogen atom, and Y is a structural unit having a polyester chain derived from a lactone compound represented by General Formula (5)



wherein R^3 is an alkylene group having a carbon number ranging from 1 to 10 which may be substituted by an aliphatic alkyl group having a carbon number ranging from 1 to 20, with a polyamine compound.

The compound having amino groups of the present invention can be prepared by the reaction of the polyester compound represented by General Formula (4) with a polyamine compound. The polyester compound represented by the general formula (4) can be prepared by a variety of methods as described below.

It is to be noted that the polyester compound represented by the general formula (4) desirably has the functional group capable of reacting with amino groups at only one terminal of the polyester chain. As the functional group capable of reacting with amino groups, (meth)acryloyl group is preferably employed from a viewpoint of industrial manufacturing and reactivity.

The polyester compound having (meth)acryloyl group at only one terminal can be prepared by the following typical three processes; (1) an addition reaction of a lactone compound to a (meth)acrylate having hydroxyl group such as hydroxyethyl(meth)acrylate, (2) a transesterification reaction of a (meth)acrylic ester with a lactone compound, and (3) an addition reaction of a polyester having carboxylic group at one terminal with a (meth)acrylate having epoxy group such as glycidylmethacrylate.

In the addition reaction (1), as the (meth)acrylate having hydroxyl group, there can be employed hydroxyethyl(meth)acrylate, hydroxypropyl(meth)acrylate, and hydroxybutyl(meth)acrylate. In the addition reaction (1), as the lactone compound, there can be employed at least one of lactone compounds represented by the general formula (5) such as epsilon-caprolactone, delta-valerolactone, beta-methyl-delta-valerolactone, 4-methylcaprolactone, 2-methylcaprolactone, beta-propiolactone, and gamma-butyrolactone.

Of those, the lactone compound having side chain such as 4-methylcaprolactone and 2-methylcaprolactone can give an excellent compatibility into resins and an excellent solubility into solvents to the resulting compound having amino group because of capability of putting out of order of crystallinity in polyester chains, preferably resulting in decreasing viscosity and keeping a stability of coatings in low temperatures.

In the addition reaction (1), the (meth)acrylate having hydroxyl group and the lactone compounds are charged into a reaction vessel equipped with a condenser, an agitator, and a tube for supplying air or oxygen, and then heated. Reaction temperature ranges from 50 to 150°C, and preferably from 80 to 120°C. In the case when the temperature is below 50°C, the reaction rate is slow and, contrarily, in the case when the temperature exceeds 150°C, the (meth)acrylate having hydroxyl group polymerizes, unpreferably resulting in incapability of preparing a desired product.

As catalysts in the addition reaction (1), there can be employed a titanium-based catalyst such as tetrabutyl titanate and tetraisopropyl titanate, tin-based catalyst such as stannous chloride, stannous octylate and monobutyltin oxide, and acids such as p-toluene sulfonic acid, and the like.

The catalyst can be employed in an amount ranging from 0.1 to 3,000 ppm, and preferably from 1 to 100 ppm. In the case when the amount is below 0.1 ppm, the reaction rate is slow and, contrarily, in the case when the amount exceeds 3,000 ppm, the polyester compound considerably colors and the excessive amount of catalyst to be employed adversely affects a stability in a product such as a coating composition.

In the addition reaction (1), a polymerization inhibitor is preferably employed in order to prevent polymerization of

the (meth)acrylate having hydroxyl group.

As the polymerization inhibitor, there can be employed hydroquinone, methylhydroquinone, and phenothiazine which are conventional polymerization inhibitors. Furthermore, the addition reaction can be preferably carried out in the presence of an appropriate amount of oxygen in order to prevent polymerization of the (meth)acrylate having hydroxyl group.

In the transesterification reaction (2), as the (meth)acrylic ester, there can be employed methyl(meth)acrylate, ethyl(meth)acrylate, butyl(meth)acrylate, and octyl(meth)acrylate.

As the lactone compound, there can be employed at least one of lactone compounds represented by the general formula (5) such as epsilon-caprolactone, delta-valerolactone, beta-methyl-delta-valerolactone, 4-methylcaprolactone, 2-methylcaprolactone, beta-propiolactone, and gamma-butyrolactone.

Of those, the lactone compound having side chains such as 4-methylcaprolactone and 2-methylcaprolactone can give an excellent compatibility into resins and an excellent solubility into solvents to the resulting compound having amino group because of capability of putting out of order of crystallinity in polyester chains, preferably resulting in decreasing viscosity and keeping a stability of coatings in low temperatures.

Even in the case when the polyester compound cannot be liquified at ordinary temperatures by the use of only the lactone compound not having side chains, it can be liquified by copolymerizing with the lactone compound having side chains.

Also in the transesterification reaction (2), the (meth)acrylate and the lactone compounds are charged into a reaction vessel equipped with a condenser, agitator, and a tube for supplying air or oxygen, and then heated. Reaction temperature ranges from 50 to 150°C, and preferably from 80 to 120°C. In the case when the temperature is below 50°C, the reaction rate is slow and, contrarily, in the case when the temperature exceeds 150°C, the (meth)acrylate polymerizes, unpreferably resulting in incapability of preparing a desired product.

As catalysts in the transesterification reaction (2), there can be employed a titanium-based catalyst such as tetrabutyl titanate and tetraisopropyl titanate, tin-based catalyst such as stannous chloride, stannous octylate and monobutyltin oxide, and acids such as p-toluene sulfonic acid, and the like.

The catalyst can be employed in an amount ranging from 0.1 to 1%, and preferably from 1 to 1000 ppm. In the case when the amount is below 0.1 ppm, the reaction rate is slow and, contrarily, in the case when the amount exceeds 1%, the polyester compound considerably colors and the excessive amount of catalyst to be employed adversely affects a stability in a product such as a coating composition.

Also in the transesterification reaction (2), a polymerization inhibitor is preferably employed in order to prevent polymerization of the (meth)acrylate.

As polymerization inhibitor, there can be employed hydroquinone, methylhydroquinone, and phenothiazine which are conventional polymerization inhibitors. Furthermore, the transesterification reaction (2) can be preferably carried out in the presence of an appropriate amount of oxygen in order to prevent polymerization of the (meth)acrylate.

A polyester having carboxylic group at one terminal in the addition reaction (3) can be prepared by an addition reaction of lactone compounds to a monocarboxylic acid or by an addition reaction of lactone compounds to a carboxylic acid having hydroxyl group.

As the monocarboxylic acid in the addition reaction (3), there can be employed at least one of aliphatic or aromatic carboxylic acids such as acetic acid, propionic acid, butyric acid, valeric acid, trimethyl acetic acid, caproic acid, lauryl acid, stearic acid, phenyl acetic acid, methoxy acetic acid, and the like.

As the lactone compound, there can be employed at least one of lactone compounds represented by the general formula (5) such as epsilon-caprolactone, delta-valerolactone, beta-methyl-delta-valerolactone, 4-methylcaprolactone, 2-methylcaprolactone, beta-propiolactone, and gamma-butyrolactone.

Of those, the lactone compound having side chains can give an excellent compatibility into resins and an excellent solubility into solvents to the resulting compound having amino group because of capability of putting out of order of crystallinity in polyester chains, preferably resulting in decreasing viscosity and keeping a stability of coatings in low temperatures.

As the carboxylic acid having hydroxyl group, there can be employed ricinoleic acid, 12-hydroxystearic acid, castor oil acid, hydrogenated castor oil acid, delta-hydroxyvaleric acid, epsilon-hydroxy caproic acid, p-hydroxyethyloxycarboxylic acid, 2-hydroxynaphthalene-6-carboxylic acid, 2,2-dimethylolpropionic acid, 2,2-dimethylolvaleric acid, 2,2-dimethylolpentanoic acid, malic acid, tartaric acid, lactic acid, glycolic acid, glucolic acid, hydroxypyruvic acid, 11-ox-hexadecanoic acid, 2-oxydodecanoic acid, and salicylic acid, and the like.

As the polyester carboxylic group at one terminal in the addition reaction (3), there can be also employed a polyester compound prepared by esterification or transesterification reaction between n mol of a dicarboxylic acid or anhydride thereof and n mol of a diol, and the lactone compounds as described hereinabove.

As the dicarboxylic acid or anhydride thereof, there can be employed maleic acid, succinic acid, glutaric acid, fumaric acid, adipic acid, sebacic acid, azelaic acid, dodecanoic acid, phthalic acid, isophthalic acid, terephthalic acid, hexahydrophthalic acid, methylhexahydrophthalic acid, tetrahydrophthalic acid, trimellitic acid, methyltetrahydroph-

thalic acid, and anhydrides thereof, and the like.

As the diols, there can be employed aliphatic alcohols having or not having side chains, alicyclic alcohols, and aromatic alcohols such as ethyleneglycol, diethyleneglycol, diethyleneglycol, 1,2-propyleneglycol, 1,3-propyleneglycol, 1,3-butyleneglycol, 1,4-butyleneglycol, neopentylglycol, 3-methylpentanediol, 1,5-pentanediol, 1,6-hexanediol, trimethylolpropane, cyclohexane dimethanol, and 1,4-dibenzylalcohol, and the like. Furthermore, there can be also employed a monoepoxide of an alpha-olefine, and the like.

The polyester carboxylic group at one terminal can be prepared in a reaction vessel equipped with a condenser, an agitator, and a tube for removing water while streaming nitrogen. In the reaction, there may be also employed appropriate solvents for removing water such as toluene and xylene. The solvents to be employed in the reaction may be removed by distillation, etc. after the completion of the reaction, or may be remained as components in products without removing.

The reaction temperature ranges from 120 to 220°C, and preferably from 160 to 210°C. In the case when the reaction temperature is below 120°C, the reaction rate is exceedingly slow and, contrarily, in the case when the temperature exceeds 210°C, there readily occur side reactions other than the addition reaction of lactone compounds such as decomposition of the lactone monomers and production of cyclic lactone dimer, etc., unpreferably resulting in being difficult in preparing a polyester having carboxylic group at one terminal which has a desired molecular weight. Furthermore, the resulting polyester readily colors up.

In the addition reaction (1), catalysts can be employed.

As the catalysts, there can be employed an organic tin-based catalyst such as tinocylate, dibutyltin oxide, dibutyltin laurate, monobutyltin hydroxybutyloxyde, a tin-based catalyst such as stannous oxide and stannous chloride, a titanium-based catalyst such as tetrabutyl titanate, tetraethyl titanate, and tetrapropyl titanate, and the like.

The catalysts can be employed in an amount ranging from 0.1 to 3000 ppm, and preferably from 1 to 100 ppm. In the case when the amount exceeds 3000 ppm, the polyester compound considerably colors and the excessive amount of catalyst employed adversely affects a stability in a product such as a coating composition and, contrarily, in the case when the amount is below 0.1 ppm, the reaction rate is exceedingly slow.

Thus-obtained polyester carboxylic group at one terminal are allowed to react with a (meth)acrylate having epoxy group to obtain the polyester compound having a functional group capable of reacting with amino groups by a Michaels addition reaction which is represented by General Formula (4).

As the (meth)acrylate having epoxy group, there are preferably employed glycidylmethacrylate, beta-methylglycidyl-methacrylate, and 2,3-epoxycyclohexylmethyl(meth)acrylate.

As the (meth)acrylate having epoxy group and the polyester carboxylic group at one terminal are charged into a reaction vessel equipped with a condenser, an agitator, and a tube for supplying air or oxygen, and then heated.

The reaction temperature ranges from 50 to 150°C, and preferably from 80 to 120°C. In the case when the reaction temperature is below 50°C, the reaction rate is exceedingly slow and, contrarily, in the case when the temperature exceeds 150°C, there readily occur polymerization of the (meth)acrylate having epoxy group, resulting in incapability of obtaining a desired polyester compound having a functional group capable of reacting with amino groups by a Michaels addition reaction. In the reaction, catalysts are employed.

As the catalysts, there are exemplified, for example, amine-based catalysts such as N,N'-dimethylbenzylamine, 2-(dimethylaminomethyl)phenol, 2,4,6-tris(dimethylaminomethyl)phenol, phosphorus-based catalysts such as triphenylphosphine, tetraphenylphosphonium, and ethyltriphenylphosphonium, etc.

The catalysts can be employed in an amount ranging from 0.1 to 3000 ppm, and preferably from 1 to 500 ppm. In the case when the amount exceeds 3000 ppm, the polyester compound considerably colors and the excessive amount of the catalyst to be employed adversely affects a stability in a product such as a coating composition and, contrarily, in the case when the amount is below 0.1 ppm, the reaction rate is exceedingly slow.

The reaction are preferably carried out in the presence of polymerization inhibitors in order to prevent polymerization of (meth)acrylic group in the (meth)acrylate having epoxy group. As the polymerization inhibitors to be employed, there are exemplified hydroquinone, methylhydroquinone, and phenothiazine, etc. which are conventional polymerization inhibitors.

Furthermore, the reaction is preferably employed in the presence of a small amount of oxygen which is an another polymerization inhibitor in order to prevent polymerization of (meth)acrylic group in the (meth)acrylates having epoxy group.

In addition to the processes (1) to (3) for the preparation of the polyester carboxylic group at one terminal, there can be also employed a process in which a monofunctional polyester having one hydroxyl group is prepared and then it is allowed to react with a bifunctional isocyanate to prepare a prepolymer, and further the prepolymer is allowed to react with the (meth)acrylates having epoxy group.

However, in the case of the process, there is readily by-produced a polyester prepared by the reaction of 2 mol of the monofunctional polyester having one hydroxyl group with 1 mol of the bifunctional isocyanate. Furthermore, in the case when the unreacted isocyanate is remained, unpreferred crosslinking reactions are caused, as the result, gelation

is unpreferably caused in a succeeding reaction process with a polyamine compound as described hereinafter.

Thus-obtained polyester compound which has a functional group capable of reacting with amino groups by a Michaels addition reaction at terminal represented by the general formula (4) has a molecular weight ranging from 100 to 20,000, preferably from 300 to 10,000, and more preferably from 500 to 5,000 on an average.

In the case when the molecular weight is below 100, a resulting compound having amino group in a succeeding reaction process with a polyamine compound cannot sufficiently form a sterically repulsive layer around pigments and, contrarily, in the case when the molecular weight exceeds 20,000, molecular weight in a resulting compound having amino group becomes excessively larger, resulting in that there decreases compatibility with a composition for coatings or inks and there also lowers dispersity of pigments.

A compound having amino groups can be prepared by the reaction of thus-obtained polyester compound having a functional group capable of reacting with amino groups by a Michaels addition reaction at terminal represented by General Formula (4) with a polyamine compound in a succeeding step.

The polyamine to be employed in the succeeding step desirably has a molecular weight ranging from 200 to 100,000.

In the case when the molecular weight is below 200, there becomes excessively low a molecular weight of an adsorptive portion in the compound having amino group, unpreferably resulting in that the use of the polyamine compound is not effective.

Contrarily, in the case when the molecular weight exceeds 100,000, molecular weight of the compound having amino groups becomes excessively larger, resulting in that the compound having amino groups tends to associate each other and the dispersity of pigments also tends to lower.

Furthermore, the melting viscosity of the compound having amino groups, becomes higher, resulting in difficulties for their preparation.

Specific examples of the polyamine to be employed include a polyethylene imine which can be prepared by a ring-opening polymerization of ethyleneimine, a polyallyl amine which can be prepared by a polymerization of allylamine, and a polyvinyl amine which can be prepared by a polymerization of vinylamine.

Furthermore, there can be also employed reaction products with a monoepoxide of an alpha-olefine, a monoepoxide of Kardula E (manufactured by Nihon Yushi Co. Ltd.), etc., a polyamine compound modified by an acrylic monomer such as methyl(meth)acrylate, butyl(meth)acrylate, hydroxyethyl(meth)acrylate, and cyclohexyl(meth)acrylate.

The polyester compound having a functional group capable of reacting with amino groups by a Michaels addition reaction at terminal is allowed to react with the polyamine compound in a ratio ranging from 1/1 to 1/99, preferably from 2/3 to 1/65 based on the molar ratio of the functional group to amino group. In the case when it exceeds 1/1, the functional group remains, unpreferably resulting in that a stability in a composition becomes poor and, contrarily, in the case when it is below 1/99, the use of the polyamine becomes meaningless.

The polyester compound having a functional group capable of reacting with amino groups and the polyamine compound are allowed to react in a reaction vessel equipped with a condenser, an agitator, and a tube for removing water.

The reaction quantitatively and quickly proceeds as a slight exothermal reaction even at room temperatures.

Accordingly, the reaction temperature ranges from 10 to 130°C, and preferably from 20 to 100°C. In the case when the temperature is below 10°C, the reaction rate is slow, resulting in incapability of industrially manufacturing and, contrarily, in the case when it exceeds 130°C, the functional groups capable of reacting with amino groups by a Michaels addition reaction react each other, and there occurs a problem that a reaction product colors up.

In the reaction, there can be also employed inert solvents not affecting the addition reaction. As examples of the solvents, there can be employed aromatic solvents such as xylene, toluene, Solvesso, ketones such as acetone, methylethylketone, methylisobutylketone, alcohols such as butanol and isopropanol, esters such as dimethyladipate, dimethylsuccinate, and dimethylglutarate.

Although the solvents employed in the reaction can be removed by evaporation after the completion of the reaction, the solvents can be employed as components in products.

The thus obtained polyester compound which has a functional group capable of reacting with amino groups by a Michaels addition reaction at terminal represented by the general formula (4) also has a molecular weight ranging from 100 to 20,000, preferably from 300 to 10,000, and more preferably from 500 to 5,000 on an average.

In the case when the molecular weight is below 100, a resulting compound having amino groups in a succeeding reaction process with a polyamine compound cannot sufficiently form a sterically repulsive layer around pigments and, contrarily, in the case when the molecular weight exceeds 20,000, molecular weight in a resulting compound having amino groups becomes excessively larger, resulting in that there decreases compatibility with a composition for coatings or inks and there also lowers dispersity of pigments.

In the thus obtained compound having amino groups of the present invention, in the case when the opposite terminal to the amino group in the polyester chain is terminated by hydroxyl group, the compound having amino group of the present invention is firmly incorporated into coated layer by the reaction with melamine resins or diisocyanate

compounds in a baking process of coatings. Accordingly, the compound having amino groups in the coated layer does not bleed out and does not crystallize, preferably resulting in that pigments grasped by the compound having amino groups do not bleed out of the coating layer and do not tend to readily aggregate.

Furthermore, the use of a lactone-contained polyester compound having a reasonable molecular weight enables to employ a relatively polar solvent such as alcohols or cellosolves for dispersing pigments.

The compound having amino groups of the present invention has an excellent dispersity for inorganic pigments such as titanium oxide, zinc oxide, cadmium sulfide, yellow iron oxide, red iron oxide, chrome yellow, carbon black, organic pigments such as phthalocyanine, insoluble azo-based dyes, azolake pigments, condensed polycyclic-based pigments (a durene-based, an indigo-based, a perylene-based, a perinone-based, a phthalone-based, a dioxadine-based, a quinacridone-based, an isoindolinone-based, and a diketopyrrolopyrrole-based pigment).

Furthermore, a millbase composition containing the compound having amino groups of the present invention is excellent in fluidity and storage stability.

For inorganic pigments, there may be generally employed a small amount of the compound having amino groups, specifically, the ratio of ranging from 1/20 to 1/200, preferably from 1/50 to 1/100. For organic pigments, there may be generally employed a relatively larger amount of the compound having amino groups, specifically, the ratio ranging from 1/1 to 1/50, preferably from 1/2 to 1/10.

In the case when the compound having amino groups is excessively employed, properties of coating layer decrease and, contrarily, in the case when the pigments are excessively less employed, a dispersing time of period becomes lengthened, and a stability in a composition becomes poor.

In the following, although the present invention is specifically illustrated below by Examples, it is not limited by the Examples. It is to be noted that the terminology "part" and "%" are based on the weight.

Example 1

Preparation No. 1 of a polylactone having amino groups represented by the general formula (1)

A 2-liter glass-made reaction flask equipped with an agitator, a Dimroth condenser, a thermometer, a tube for blowing air was charged with 232 parts of hydroxyethylacrylate (HEA), 684 parts of epsilon-caprolactone, 0.009 part of stannous chloride, 1 part of methylhydroquinone, followed by heating at 100°C to allow to react until epsilon-caprolactone monomer decreases to less than 1% to obtain a lactone-modified hydroxyethylacrylate. successively, the temperature was lowered to 50°C, and then 86 parts of piperazine was added while stirring to allow to react.

The reaction was terminated by monitoring with an ¹H-NMR analyzer that acrylic group disappeared to obtain a polylactone having amino groups.

Delta value (ppm) in ¹H-NMR

1.3-1.5:	multiplet by methylene proton in polycaprolactone (12H)
1.5-1.8:	multiplet by methylene proton in polycaprolactone (24H)
2.2-2.4:	multiplet by methylene proton in polycaprolactone (12H)
2.4-2.6:	multiplet by methylene proton in piperazine, -CH ₂ -CO- (12H)
2.7:	triplet by methylene proton in -N-CH ₂ CH ₂ -CO- (4H)
3.6:	triplet by methylene proton in polycaprolactone (-CH ₂ -OH) (4H)
3.75:	triplet by methylene proton of the bonded OH in HEA added to piperazine
4.05:	triplet by methylene proton in polycaprolactone (-CH ₂ -OCO-) (12H)
4.3:	singlet by methylene proton in -COOCH ₂ CH ₂ -O- (8H)

It was identified by the assignment of the delta values in the ¹H-NMR analysis that the polylactone has the chemical formula represented by General Formula (1) as described below;



wherein R¹ is -CH₂CH₂-COOCH₂CH₂O-[-CO(CH₂)₅O-]₂-CO(CH₂)₅-OH.

Furthermore, it was identified that the polylactone having amino groups which is a liquid exhibits a hydroxyl value of 112 mgKOH/g and APHA value (color hue) of 80.

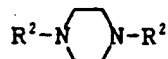
Example 2

Preparation No. 2 of a polylactone having amino groups represented by the general formula (1)

- 5 The same procedures were followed as in Example 1, except that there were employed 288 parts of hydroxybuty-lacrylate (HBA), 1140 parts of epsilon-caprolactone, and 0.01 part of monobutyltin oxide. The reaction was terminated by monitoring with an $^1\text{H-NMR}$ analyzer that acrylic group disappeared to obtain a polylactone having amino groups. Delta value (ppm) in $^1\text{H-NMR}$

- 10 1.3-1.5: multiplet by methylene proton in polycaprolac tone (10H)
 1.5-1.8: multiplet by methylene proton in polycaprolac tone (48H)
 2.2-2.4: multiplet by methylene proton in polycaprolac tone (20H)
 2.4-2.6: multiplet by methylene proton in piperazine, $-\text{CH}_2-\text{CO}-$ (20H)
 2.7: triplet by methylene proton in $-\text{N}-\text{CH}_2\text{CH}_2-\text{CO}-$ (4H)
 15 3.6: triplet by methylene proton in polycaprolactone ($-\text{CH}_2-\text{OH}$) (4H)
 3.75: triplet by methylene proton of the bonded OH in HBA added to piperazine
 4.05: triplet by methylene proton in polycaprolactone ($-\text{CH}_2-\text{OCO}-$) (8H)
 4.3: triplet by methylene proton in $-\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{O}-$ (8H)

- 20 It was identified by the assignment of the delta values in the $^1\text{H-NMR}$ analysis that the polylactone having amino groups exhibits the chemical formula represented by General Formula (1) as described below;



- 25 wherein R^2 is $-\text{CH}_2\text{CH}_2-\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-[\text{CO}(\text{CH}_2)_5\text{O}]_4-\text{CO}(\text{CH}_2)_5-\text{OH}$.

Furthermore, it was identified that the polylactone having amino groups which is a viscous liquid has a hydroxyl value of 75 mgKOH/g and AHA value (color hue) of 110.

Example 3

30

Preparation No. 3 of a polylactone having amino groups represented by the general formula (1)

- The same procedures were followed as in Example 1, except that there were employed 232 parts of hydroxyethy-lacrylate (HEA), 684 parts of epsilon-caprolactone, 0.02 part of stannous chloride, 2 part of methylhydroquinone, and 100 parts of 2-methylpiperazine. The reaction was terminated by monitoring with an $^1\text{H-NMR}$ analyzer that acrylic group disappeared to obtain a polylactone having amino groups. Delta value (ppm) in $^1\text{H-NMR}$

- 1.0-1.2: doublet by methylene proton in piperazine (3H)
 40 1.3-1.5: multiplet by methylene proton in polycaprolac tone (12H)
 1.5-1.8: multiplet by methylene proton in polycaprolac tone (24H)
 2.2-2.4: multiplet by methylene proton in polycaprolac tone (12H)
 2.4-2.6: multiplet by methylene proton in piperazine, $-\text{CH}_2-\text{CO}-$ (11H)
 2.7: triplet by methylene proton in $-\text{N}-\text{CH}_2\text{CH}_2-\text{CO}-$ (4H)
 45 3.6: triplet by methylene proton in polycaprolactone (4H)
 3.75: triplet by methylene proton of the bonded OH in HEA added to piperazine
 4.05: triplet by methylene proton in polycaprolactone ($-\text{CH}_2-\text{OCO}-$) (8H)
 4.3: triplet by methylene proton in $-\text{COOCH}_2\text{CH}_2-\text{O}-$ (8H)

- 50 It was identified by the assignment of the delta values in the $^1\text{H-NMR}$ analysis that the polylactone having amino groups exhibits the chemical formula represented by General Formula (1) as described below;



- 55 wherein R^3 is $-\text{CH}_2\text{CH}_2-\text{COOCH}_2\text{CH}_2\text{O}-[\text{CO}(\text{CH}_2)_5\text{O}]_2-\text{CO}(\text{CH}_2)_5-\text{OH}$.

Furthermore, it was identified that the polylactone having amino groups which is a highly viscous liquid has a hydroxyl value of 109 mgKOH/g and AHA value (color hue) of 90.

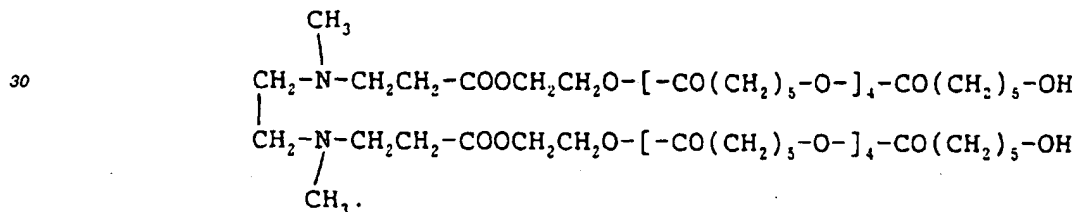
Example 4

Preparation No. 4 of a polylactone having amino groups represented by the general formula (1)

- 5 A 5-liter glass-made reaction flask equipped with an agitator, a Dimroth condenser, a thermometer, a tube for blowing air was charged with 232 parts of hydroxyethylacrylate (HEA), 1140 parts of epsilon-caprolactone, 0.02 part of stannous chloride, 2 part of methylhydroquinone, followed by heating at 100°C to allow to react until epsilon-caprolactone decreases to less than 1% to obtain a lactone-modified hydroxyethylacrylate. Successively, the temperature was lowered to 50°C, and then 88 parts of N,N'-dimethylethylenediamine ($\text{CH}_3\text{-NH-CH}_2\text{CH}_2\text{-NHCH}_3$) was added while stirring. The reaction was terminated by monitoring with an $^1\text{H-NMR}$ analyzer that acrylic group disappeared to obtain a polylactone having amino groups.
Delta value (ppm) in $^1\text{H-NMR}$

- 1.3-1.5: multiplet by methylene proton in polycaprolactone (20H)
15 1.5-1.8: multiplet by methylene proton in polycaprolactone (40H)
2.2-2.4: multiplet by methylene proton in polycaprolactone (20H)
2.4-2.6: multiplet by methylene proton in $-\text{N-CH}_2-$, $-\text{CO-CH}_2-$ (6H)
2.7: triplet by methylene proton in $-\text{N-CH}_2\text{CH}_2\text{-CO-}$ (4H)
3.6: triplet by methylene proton of $-\text{CH}_2\text{-OH}$ in polycaprolactone (4H)
20 3.75: triplet by methylene proton of the bonded OH in HEA added to N,N'-dimethylethylenediamine
4.05: triplet by methylene proton of $-\text{CH}_2\text{-OCO-}$ in polycaprolactone (12H)
4.3: singlet by methylene proton in $-\text{CO-OCH}_2\text{CH}_2\text{-O-}$ (8H)
1.8-2.0: singlet by methylene proton in $-\text{N-CH}_3$ (6H)

- 25 It was identified by the assignment of the delta values in the $^1\text{H-NMR}$ analysis that the polylactone having amino groups exhibits the chemical formula represented by General Formula (1) as described below;



Furthermore, it was identified that the polylactone having amino groups which is a highly viscous liquid has a hydroxyl value of 77 mgKOH/g and APHA value (color hue) of 130.

Example 5

- 40 Preparation No. 5 of a polylactone having amino groups represented by the general formula (1)

- The same procedures were followed as in Example 1, except that there were employed 1140 parts of epsilon-caprolactone, 0.02 part of stannous chloride, and 2 parts of methylhydroquinone to obtain a lactone-modified hydroxyethylacrylate.

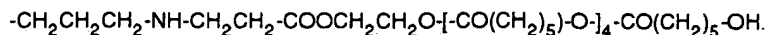
- 45 Successively, the temperature was lowered to 50°C, and then 200 parts of 1,4-bis(3-aminopropyl)piperazine was added while stirring. The reaction was terminated by monitoring with an $^1\text{H-NMR}$ analyzer that acrylic group disappeared to obtain a polylactone having amino groups.
Delta value (ppm) in $^1\text{H-NMR}$

- 50 2.2-2.8: multiplet by methylene proton in $-\text{N-CH}_2-$ (20H)
1.5-1.8: multiplet by methylene proton in $\text{N-CH}_2\text{CH}_2\text{CH}_2\text{-N}$ (4H)
2.4-2.6: multiplet by methylene proton in $-\text{N-CH}_2\text{CH}_2\text{COO}$ (4H)
4.3: singlet by methylene proton in $-\text{CO-O-CH}_2\text{CH}_2\text{-O-}$ (8H)
55 1.3-1.5: multiplet by methylene proton in polycaprolactone (20H)
1.5-1.8: multiplet by methylene proton in polycaprolactone (40H)
2.2-2.4: multiplet by methylene proton in polycaprolactone (20H)
3.6: multiplet by methylene proton in $-\text{CH}_2\text{OH}$ (4H)

It was identified by the assignment of the delta values in the $^1\text{H-NMR}$ analysis that the polylactone having amino groups exhibits the chemical formula represented by General Formula (1) as described below;



wherein R^5 is



Furthermore, it was identified that the polylactone having amino groups which is a viscous liquid has APHA value (color hue) of 120.

Comparative Example 1

Preparation No. 6 of a polylactone having amino groups

A 2-liter glass-made reaction flask equipped with an agitator, a Dimroth condenser, a thermometer, and a tube for blowing air was charged with 1140 parts of epsilon-caprolactone, 0.02 part of stannous chloride, and 200 parts of 1,4-bis(3-aminopropyl)piperazine, followed by heating at 150°C to allow to react until epsilon-caprolactone decreases to less than 1% to obtain a waxy brown-colored polylactone having APHA of more than 500.

Comparative Example 2

Preparation No. 7 of a polylactone having amino groups

The same procedures were followed as in Comparative Example 1, except that there was employed 119 parts of N-methyldiethanolamine to obtain a brown-colored polylactone having amino groups having APHA of more than 500 which is a brown-colored high viscous liquid.

Preparation Example 1

Preparation No. 1 of a polyester compound represented by the general formula (4)

A 2-liter glass-made reaction flask equipped with an agitator, a Dimroth condenser, a thermometer, and a tube for blowing air was charged with 116 parts of hydroxyethylacrylate, 1140 parts of epsilon-caprolactone, 0.012 part of monobutyltin oxide, and 1.3 part of methylhydroquinone, followed by heating at 100°C for 10 hours to allow to react until epsilon-caprolactone decreases to less than 1% to obtain a polyester compound represented by General Formula (4).

The polyester compound is designated as PE-1.

Preparation Example 2

<Preparation No. 2 of a polyester compound represented by General Formula (4)>

The same procedures were followed as in Preparation Example 1, except that 1710 parts of epsilon-caprolactone, 0.018 part of monobutyltin oxide, and 1.8 part of methylhydroquinone were employed to obtain a polyester compound represented by General Formula (4).

The polyester compound is designated as PE-2.

Preparation Example 3

Preparation No. 3 of a polyester compound represented by the general formula (4)

The same procedures were followed as in Preparation Example 1, except that 3-liter glass-made reaction flask 2280 parts of epsilon-caprolactone, 0.025 part of monobutyltin oxide, and 2.5 part of methylhydroquinone were employed to obtain a polyester compound represented by General Formula(4). The polyester compound is designated as PE-3.

Preparation Example 4

Preparation No. 4 of a polyester compound represented by the general formula (4)

- 5 The same procedures were followed as in Preparation Example 1, except that 3-liter glass-made reaction flask, 130 parts of hydroxyethylacrylate, 1710 parts of epsilon-caprolactone, 0.020 part of monobutyltin oxide, and 2.0 part of methylhydroquinone were employed to obtain a polyester compound represented by General Formula (4). The polyester compound is designated as PE-4.

10 Preparation Example 5

Preparation No. 5 of a polyester compound represented by the general formula (4)

- 15 The same procedures were followed as in Preparation Example 1, except that 3-liter glass-made reaction flask, 1400 parts of epsilon-caprolactone, 600 parts of 4-methylcaprolactone, 0.021 part of monobutyltin oxide, and 2.1 part of methylhydroquinone to obtain a polyester compound represented by General Formula (4). The polyester compound is designated as PE-5.

20 Preparation Example 6

Preparation No. 6 of a polyester compound represented by General Formula (4)

- 25 The same procedures were followed as in Preparation Example 1, except that 3-liter glass-made reaction flask, 1600 parts of epsilon-caprolactone, 400 parts of 4-methylcaprolactone, 0.021 part of monobutyltin oxide, and 2.1 part of methylhydroquinone to obtain a polyester compound represented by General Formula (4). The polyester compound is designated as PE-6.

Preparation Example 7

- 30 Preparation No. 7 of a polyester compound represented by the general formula (4)

- A 3-liter glass-made reaction flask equipped with an agitator, a Dimroth condenser, a thermometer, and a tube for blowing air was charged with 116 parts of caproic acid, 1400 parts of epsilon-caprolactone, 600 parts of 12-hydroxy-stearic acid, and 0.05 part of tetrabutyl titanate, followed by heating at 190°C for 14 hours to allow to react to obtain a
35 polyester compound represented by General Formula (4) which is a viscous liquid having an acid value of 28 mgKOH/g. Successively, the polyester compound was cooled to 80°C, and 1 part of triphenylphosphine as a catalyst was dissolved, and then 142 parts of glycidylmethacrylate was added dropwise to allow to react until the acid value changes to 1 mgKOH/g.

- 40 The glycidylmethacrylate-modified polyester compound is designated as PE-7.

Example 6

<Preparation No. 1 of a compound having amino groups>

- 45 A 2-liter glass-made reaction flask equipped with an agitator, a Dimroth condenser, a thermometer, and a tube for blowing air was charged with 900 parts of PE-1, followed by heating at 60°C. Successively, there was charged 100 parts of a polyethyleneimine having a molecular weight of 10,000 (SP200, manufactured by Nihon Shokubai Kagaku Co. Ltd.) to allow to react while stirring. Reaction was terminated after monitoring that acrylic groups disappeared with a proton NMR analyzer.

- 50 Reaction product was a waxy solid having an amino value of 102 mgKOH/g and an APHA value of 130 in a melting state.

The waxy solid was designated as CAG-1.

Example 7

55

Preparation No. 2 of a compound having amino groups

The same procedures were followed as in Example 6, except that 950 parts of PE-1 and 50 parts of SP200 were

employed to obtain a waxy solid having an amino value of 55 mgKOH/g and an APHA value of 120 in a melting state.
The waxy solid was designated as CAG-2.

Example 8

Preparation No. 3 of a compound having amino groups

The same procedures were followed as in Example 6, except that 900 parts of PE-2 and 100 parts of SP200 were employed to obtain a waxy solid having an amino value of 105 mgKOH/g and an APHA value of 130 in a melting state.
The waxy solid was designated as CAG-3.

Example 9

Preparation No. 4 of a compound having amino groups

The same procedures were followed as in Example 6, except that 950 parts of PE-2 and 50 parts of SP200 were employed to obtain a waxy solid having an amino value of 54 mgKOH/g and an APHA value of 120 in a melting state.
The waxy solid was designated as CAG-4.

Example 10

Preparation No. 5 of a compound having amino groups

The same procedures were followed as in Example 6, except that 950 parts of PE-3 and 50 parts of SP200 were employed to obtain a waxy solid having an amino value of 55 mgKOH/g and an APHA value of 190 in a melting state.
The waxy solid was designated as CAG-5.

Example 11

Preparation No. 6 of a compound having amino groups

The same procedures were followed as in Example 6, except that 900 parts of PE-2 and 100 parts of a polyethyleneimine having a molecular weight of 1,800 (SP018, manufactured by Nihon Shokubai Kagaku Co. Ltd.) were employed to obtain a waxy solid having an amino value of 104 mgKOH/g and an APHA value of 200 in a melting state.
The waxy solid was designated as CAG-6.

Example 12

Preparation No. 7 of a compound having amino groups

The same procedures were followed as in Example 6, except that 950 parts of PE-2 and 50 parts of SP018 were employed to obtain a waxy solid having an amino value of 55 mgKOH/g and an APHA value of 180 in a melting state.
The waxy solid was designated as CAG-7.

Example 13

Preparation No. 8 of a compound having amino groups

The same procedures were followed as in Example 6, except that 900 parts of PE-4 and 100 parts of SP018 were employed to obtain a waxy solid having an amino value of 100 mgKOH/g and an APHA value of 150 in a melting state.
The waxy solid was designated as CAG-8.

Example 14

Preparation No. 9 of a compound having amino groups

The same procedures were followed as in Example 6, except that 900 parts of PE-5 and 100 parts of SP200 were employed to obtain a viscous liquid having an amino value of 102 mgKOH/g and an APHA value of 120 in a melting

state. The viscous liquid was designated as CAG-9.

Example 15

5 Preparation No. 10 of a compound having amino groups

The same procedures were followed as in Example 6, except that 900 parts of PE-6 and 100 parts of SP018 were employed to obtain a viscous liquid having an amino value of 104 mgKOH/g and an APHA value of 180 in a melting state. The viscous liquid was designated as CAG-10.

10

Example 16

Preparation No. 11 of a compound having amino groups

15 The same procedures were followed as in Example 6, except that 900 parts of PE-7 and 100 parts of SP200 were employed to obtain a waxy solid having an amino value of 99 mgKOH/g and an APHA value of 250 in a melting state. The waxy solid was designated as CAG-11.

Example 17

20

Preparation No. 12 of a compound having amino groups

The same procedures were followed as in Example 6, except that 950 parts of PE-4 was employed and 200 parts of xylene was charged to dissolve, followed by heating at 40°C, and then 50 parts of SP200 was charged to obtain a reaction product.

25

200 g of tetrahydrofuran was charged into the reaction product while sufficiently stirring to dissolve. Successively, 90 parts of dimethyl sulfate was charged and sufficiently mixed, followed by heating at 60°C while stirring for 2 hours.

Subsequently, xylene employed in the reaction was removed at 80°C under reduced pressures to obtain a solid product. The solid product was designated as CAG-12.

30

Comparative Example 3

Preparation No. 1 of a polyester compound having amide units

35 A 3-liter glass-made reaction flask equipped with an agitator, a condenser, thermometer, and a tube for blowing nitrogen was charged with 116 parts of caproic acid, 2000 parts of epsilon-caprolactone, and 2 parts of tetrabutyl titanate, followed by heating at 185°C for 18 hours while streaming nitrogen gas to allow to react to obtain a polyester compound.

40 A 2-liter glass-made reaction flask equipped with an agitator, a condenser, thermometer, a tube for removing water, and a tube for blowing nitrogen was charged with 1000 parts of the above-described polyester compound. Successively, there were charged 100 parts of a polyethyleneimine having a molecular weight of 10,000 (SP200, manufactured by Nihon Shokubai Kagaku Co. Ltd.) and 600 cm³ of toluene as a solvent for removing water to allow to react while stirring at 150°C.

Reaction was terminated at the period that 14 cm³ of water was removed to obtain a toluene solution product.

45 Amino value of the product after removing toluene was 70 mgKOH/g. APHA value in a melting state was 500.

Furthermore, absorption peaks by amide bonds were observed at 1650 cm⁻¹ and 1550 cm⁻¹ in IR spectra, whereby, it was identified that a polyester chain is grafted to polyethyleneimine through amide bond. The product was designated as CAG-13.

Application Example 1: Fluidity test No. 1

50 In an apparatus (manufactured by Reddevil, Ltd.) for dispersing, there were mixed 75 parts of titanium oxide (Type-hk CR95:C.I-Pigment White 6 manufactured by Ishihara Sangyo), 1 part of the compound having amino group obtained in Example 6, 7 parts of xylene, 7 parts of butylcellosolve acetate, and 100 parts of glass beads for 60 minutes to obtain a dispersed paste.

55

The dispersed paste exhibited a good fluidity at even after 1 week.

Application Examples 2-22: Fluidity test Nos. 2-22

In the same apparatus as in Application Example 1, there were mixed respective pigments, the compounds having amino group obtained in Examples 6-17, xylene, butylcellosolve acetate, and 100 parts of glass beads for 60 minutes to obtain respective dispersed pastes, based on respective mixing ratio as described in Table 1. The dispersed pastes exhibited a good fluidity at even after 1 week.

Table 1

	Application	Pigment	Compound having amino group	Solvent
	Example 2	A (20)	CAG-1 (4)	Xylene (38)/BCA (38)
	3	B (25)	CAG-1 (10)	Xylene (32.5)/BCA (32.5)
	4	C (75)	CAG-2 (1)	Xylene (7)/BCA (7)
	5	A (20)	CAG-2 (4)	Xylene (23)/BCA (23)
	6	B (25)	CAG-2 (10)	Xylene (32.5)/BCA (32.5)
	7	C (75)	CAG-3 (1)	Xylene (7)/BCA (7)
	8	A (20)	CAG-3 (4)	Xylene (23)/BCA (23)
	9	B (25)	CAG-3 (10)	Xylene (32.5)/BCA (32.5)
	10	D (25)	CAG-7 (10)	Xylene (65)
	11	E (45)	CAG-8 (5)	Xylene (50)
	12	F (60)	CAG-9 (2)	Xylene (38)
	13	G (70)	CAG-10 (2)	Xylene (14)/BCA (14)
	14	H (40)	CAG-2 (2)	MIBK (29)/BCA (29)

	15	I (45)	CAG-2 (2.5)	Xylene (52.75)
5	16	J (40)	CAG-4 (2)	Xylene (5)
	17	K (20)	CAG-5 (10)	Xylene (70)
	18	K (20)	CAG-6 (10)	Xylene (70)
10	19	K (20)	CAG-9 (10)	Xylene (70)
	20	L (45)	CAG-3 (3)	Xylene (52)
15	21	K (20)	CAG-7 (10)	Xylene (70)
	22	I (45)	CAG-12 (2)	Xylene (53.25)

20 In the Table 1, numerical values in parenthesis represent parts by weight of respective components, and alphabetical indications or abbreviations are as follows.

- 25 A: Carbon black (MA-100:C.I-Pigment Black 7 manufactured by Mitsubishi Kasei Co.)
 B: Phthalocyanineblue (Chlomofineblue 4920:C.I-Pigment Blue 15:3 manufactured by Dainichi Seika Kogyo)
 C: Titanium oxide (Typehk CR95:C.I-Pigment White 6 manufactured by Ishihara Sangyo)
 D: Phthalocyanineblue (Chlomofineblue 5310:C.I-Pigment Green 7 manufactured by Dainichi Seika Kogyo)
 E: Benzimidazolone Yellow (Chlomofineyellow 2080:C.I-Pigment Yellow 154 manufactured by Dainichi Seika Kogyo)
 F: Yellow iron oxide (Mapicoyellow LLXLO:C. I-Pigment Yellow 42 manufactured by Titanium Kogyo)
 30 G: Red iron oxide (C.I-Pigment Red 101)
 H: Quinacridone (Chlomofine red 6820:C.I-Pigment Violet 19 manufactured by Dainichi Seika Kogyo)
 I: Brilliant Carmin 6B (Similer Brilliant Carmin 6B 236:C. I-Pigment Red 57:1 manufactured by Dainippon Ink Kagaku Kogyo)
 J: Disazoyellow (Seikafastyellow 2300:C. I-Pigment Yellow 12 manufactured by Dainichi Seika Kogyo)
 35 K: Carbon black (Degussa FW-200:C. I-Pigment Black 7)
 L: Diketopyrrolopyrrole (Ciba Geigy DPP Red BO:C. I-Pigment Red 254)
 BCA: Butylcellosolve acetate
 MIBK: Methylisobutylketone

40 Comparative Application Example 1: Fluidity test No. 23

In an apparatus (manufactured by Reddevil, Ltd.) for dispersing, there were mixed 20 parts of carbon black (Degussa FW-200:C. I-Pigment Black 7), 10 parts of CAG-13, 70 parts of xylene, and 100 parts of glass beads for 60 minutes to obtain a dispersed paste. The dispersed paste exhibited fluidity immediately after dispersion. However, it exhibited a jelly state after 1 week, and did not exhibit fluidity.

Comparative Application Example 2: Fluidity test No. 24

50 In an apparatus (manufactured by Reddevil, Ltd.) for dispersing, there were mixed 20 parts of carbon black (Degussa FW-200:C. I-Pigment Black 7), 12.5 parts of an alkyd resin (Bekkozole EZ-3530-80 manufactured by Dainihon Ink Ltd. which has nonvolatile components of 80% in xylene), 67.5 parts of xylene, and 100 parts of glass beads for 60 minutes to obtain a dispersed paste. The dispersed paste exhibited a jelly state, and did not exhibit fluidity at all.

Application Examples 35, 36 and Comparative Application Example 3

55

Evaluation of coating layers was carried out using compositions in which pastes prepared in the Fluidity test Nos. 3, 19, and 23 were mixed with components as shown in Table 2 to obtain respective coating compositions.

The respective coating compositions were coated immediately after prepared and after placed at 0°C for 3 days,

and coating layers were baked at conditions of 135°C and 30 minutes to evaluate the gloss of surface (at the angle of 60 degree).

Results are shown in Table 3.

Table 2

Components	Mixing Ratio (%)
Millbase composition (a mixture composed of a pigment and a compound having amino groups)	12.6
Alkyd resin	52.2
Melamine resin	10.4
Xylene	24.0
Catalyst for curing	0.8

As the alkyd resin, there was employed Bekkozole EZ-3530-80 manufactured by Dainihon Ink, Ltd.

As the melamine resin, there was employed a methylated melamine resin manufactured by Mitsui Toatsu Kagaku, Ltd.

As the catalyst for curing, there was employed a curing accelerator manufactured by Mitsui Toatsu Kagaku, Ltd.

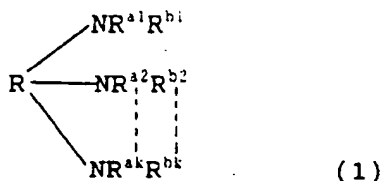
Table 3

	Gloss immediately after mixing	Gloss after 3 days after mixing
Application Example 35	94	90
Application Example 36	95	95
Comparative Application Example 3	90	81

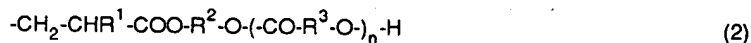
While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. A polylactone having amino groups represented by General Formula (1)



wherein R is a residual group of an aliphatic, alicyclic, or aromatic hydrocarbon, the atom N may form a ring together with said R which may have a substituent group, at least one of R^{a1} , R^{a2} , ..., R^{ak} , R^{b1} , R^{b2} , ..., R^{bk} is a substituent group represented by the general formula (2)

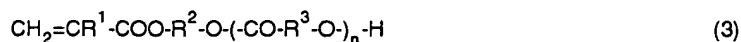


wherein R^1 is a hydrogen or methyl group, R^2 is a residual group of an aliphatic or aromatic hydrocarbon having a carbon number ranging from 1 to 10, polypropyleneoxy units or polyethyleneoxy units which may have substituent groups, R^3 is an alkylene unit having a carbon number ranging from 3 to 10 which may have side chains having a carbon number ranging from 1 to 5, n pieces of R^3 may be identical or different from each other, n is a number ranging from 1 to 100 on an average, and other R^{a1} , R^{a2} , ..., R^{ak} , R^{b1} , R^{b2} , ..., R^{bk} are independently a hydrogen or an alkyl group having a carbon number ranging from 1 to 10, k is an integer ranging from 1 to 5.

2. A polylactone having amino groups as set forth in claim 1, wherein said polylactone is derived from at least one selected from the group consisting of epsilon-caprolactone, methylcaprolactone, methylcaprolactone, delta-valerolactone, and beta-methyl-delta-valerolactone.
3. A polylactone having amino groups as set forth in claim 1 or 2, wherein said amino groups are derived from pip-

erazine or a piperazine derivative having at least two primary or secondary amino groups.

4. A process for the preparation of a polylactone having amino groups as set forth in one of claims 1 to 3 which comprises a Michaels addition reaction of a polylactone having (meth)acrylic group represented by the general formula (3)



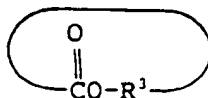
wherein R¹ is a hydrogen or methyl group, R² is a residual group of an aliphatic, alicyclic, or aromatic hydrocarbon having a carbon number ranging from 1 to 10, polypropyleneoxy units or polyethyleneoxy units which may have substituent groups, R³ is an alkylene group having a carbon number ranging from 3 to 10 which may have side chains having a carbon number 1 to 5, n pieces of R³ may be identical or different from each other, n is a number of 1 to 100 on an average, with an amine having a primary amino group or secondary amino group.

5. A process for the preparation of a polylactone having amino groups as set forth in claim 4, wherein said amine is at least one selected from the group consisting of piperazine, 1,4-bis(aminopropyl)piperazine, 2-methylpiperidine, and N,N'-dimethylethylenediamine.

6. A compound having amino groups prepared by the reaction of a polyester compound represented by the general formula (4)



wherein X is a structural unit having a functional group capable of reacting with amino groups by a Michaels addition reaction at terminal, R⁴ is an alkyl group having a carbon number ranging from 1 to 20, an aromatic group, hydroxyl group, cyano group, and halogen atom, and Y is a structural unit having a polyester chain derived from a lactone compound represented by the general formula (5)



wherein R³ is an alkylene group having a carbon number ranging from 1 to 10 which may be substituted by an aliphatic alkyl group having a carbon number ranging from 1 to 20, with a polyamine compound.

7. A compound having amino groups as set forth in claim 6, wherein said polyester compound is at least one selected from the group consisting of a lactone modified-hydroxyethyl(meth)acrylate, a lactone modified-hydroxypropyl(meth)acrylate, and a lactone modified-hydroxybutyl(meth)acrylate.

8. A compound having amino groups as set forth in claim 6 or 7, wherein said polyester compound is a compound prepared by transesterification of an alkyl(meth)acrylate with a lactone compound.

9. A compound having amino groups as set forth in one of claims 6 to 8, wherein said polyester compound is a compound prepared by the reaction of a polyester having one carboxylic group at terminal with a (meth)acrylate having epoxy group.

10. A compound having amino groups as set forth in claim 9, wherein said polyester having one carboxylic group at terminal is a compound prepared by the reaction of a carboxylic acid with a lactone compound.

11. A dispersant for pigments comprising a compound of claim 6.

12. A composition for printing inks comprising a compound of claim 6, resins for printing inks, pigments, and optionally solvents and/or curing agents.

13. A composition for printing inks as set forth in claim 12, wherein said resins for printing inks are alkyd resins or oil-free alkyd resins and melamine resins.

14. A composition for printing inks as set forth in claim 12, wherein said resins for printing inks are alkyd resins or oil-free alkyd resins and a urethane prepolymer.

15. A composition for printing inks as set forth in claim 12, wherein said resins for printing inks are acrylic resins or

epoxy resins.

- 5
16. A composition for coatings comprising a compound of claim 6, resins for coatings, and pigments, and optionally solvents and/or curing agents.
17. A composition for coatings as set forth in claim 16, wherein said resins for coatings are alkyd resins or oil-free alkyd resins and melamine resins.
- 10
18. A composition for coatings as set forth in claim 16, wherein said resins for coatings are alkyd resins or oil-free alkyd resins and a urethane prepolymer.
19. A composition for coatings as set forth in claim 16, wherein said resins for coatings are acrylic resins or epoxy resins.

15

20

25

30

35

40

45

50

55

THIS PAGE BLANK (USPTO)